THE FORMATION OF CONDENSATION NUCLEI IN CITY AIR, BY ULTRAVIOLET RADIATION OF WAVELENGTH GREATER THAN 2900A

Thesis

Submitted by

Aodhagan F. Roddy, M.Sc. (N.U.I)

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C O N T E N T S

Chapter Page

7. EXPERIMENTS IN INVESTIGATING THE TRACE GAS HYPOTHESIS

Chapter Page

GENERAL INTRODUCTION

In the initial stages of condensation of water vapour in the atmosphere, an important part is played by minute particles contained in the air, which act as nuclei, or centres of condensation. John Aitken[1], a Scottish scientist, who lived from 1839 to 1919, carried out much of the pioneer research on these minute particles, now commonly called condensation nuclei. He showed that clouds of water droplets do not normally form in air unless condensation nuclei exist to act as centres of condensation. Condensation nuclei range in size from about 10^{-3} cm. to 10^{-7} cm., and they can remain suspended in the atmosphere for a long time since their velocities of fall are very small.

Theory

The equilibrium vapour pressure p_r over the surface of a droplet of pure water, of radius r, exceeds the saturation vapour pressure, which is the vapour pressure p_∞ over a plane water surface, at the same temperature, according to the equation

$$p_r/p_\infty = \mathrm{Exp}(2\Upsilon M/\rho RTr) \qquad (1)$$

where Υ, ρ, M are respectively the surface tension, density and molecular weight of water, R the Universal gas constant, and T the absolute temperature. Thus, if such a droplet is to remain in equilibrium with its surroundings, neither evaporating nor

growing, the vapour pressure of the surrounding air must equal p_r as given by equation (1), and the surrounding air will therefore be supersaturated. The degree of supersaturation is $(p_r - p_\infty)/p_\infty$ and is usually expressed as a percentage. The degree of supersaturation required for equilibrium will be higher, the smaller the droplet. For pure water droplets of radii 10^{-3} cm., 10^{-4} cm., 10^{-5} cm., 10^{-6}., the degrees of supersaturation for equilibrium given by Mason[2], are 0.01%, 0.12%, 1.2% and 12.5% respectively. These values then show the supersaturations which must be exceeded for continued condensation to occur on pure water droplets of various sizes. For insoluble, wettable nuclei of the same sizes, the supersaturations required for condensation, will be slightly less, while those required for hydrophobic or water repellant nuclei will be slightly higher. If a droplet is formed on a soluble nucleus, the equilibrium vapour pressure at its surface is reduced by an amount depending on the nature and concentration of the solute, so that condensation and growth sets in at a lower supersaturation than that required for an insoluble particle of the same size. The equilibrium vapour pressure, p'_r, over a droplet of pure solution of radius r is given very nearly by the equation

$$p'_r/p_\infty = \exp(2\gamma M/\rho RTr)\left(1 - \frac{8.6m}{M_1 r^3}\right) \qquad (2)$$

where m is the mass of the dissolved solute in grammes, M_1 the molecular weight of the salt, the other symbols being the same as in equation (1).

Atmospheric Condensation Nuclei:

The greater part of atmospheric condensation nuclei is a mixture of various sizes of the above basic types of nuclei, having grown by mutual coagulation and condensation. They thus require various supersaturations for activation. Twomey[3] showed that only a small fraction, normally one tenth to one hundredth of the atmospheric nuclei present, are activated in the processes of cloud formation, in the atmosphere. During cloud formation in the atmosphere, the supersaturation of water vapour rarely exceeds a fraction of 1%. The most important nuclei in natural cloud formation are the large water-soluble hygroscopic nuclei.

Condensation nuclei may carry electric charges of either sign. Thus they contribute to the electrical conductivity of the atmosphere. In this sphere of action, the small nuclei have a greater effect than the large nuclei, because they have the greater mobility.

Small nuclei also play an important part in other atmospheric phenomena, such as fogs, smogs and hazes. Went[4] has discussed the formation of blue or summer haze over vegetation, whereas Haagen-Smith[5] and Leighton[6] have described the haze formed in the polluted air of cities. Small nuclei are less easily "washed out" of the atmosphere by precipitation, than the large nuclei, as they follow the aerodynamic streamlines around falling precipitation elements, due to their small momentum, whereas large nuclei often suffer coalescence with the falling precipitation element, and are removed from the atmosphere.

Small nuclei stay suspended in the atmosphere for a longer time than large nuclei, on average, due to their smaller velocities of fall.

The Concentration of Atmospheric Nuclei:

The concentration of atmospheric condensation nuclei varies enormously from place to place and from time to time. The concentration of nuclei is generally low over the oceans and over uninhabited rural areas, the concentration usually being of the order of hundreds of nuclei per c.c. of air. A concentration of 2 nuclei per c.c. has been recorded over an ocean. At the other extreme, a concentration of four million nuclei per c.c. has been recorded in a centre of great industrial activity and the concentration of nuclei is invariably much higher in densely populated areas, then in rural areas.

Sources of Atmospheric Condensation Nuclei:

It is of great interest to know the sources and modes of formation of condensation nuclei in the atmosphere. Particles capable of acting as condensation nuclei may be formed in many different ways, but these may be roughly divided into two main classes:

(1) The mechanical disruption and dispersal of bulk matter, as fine dust or spray.

(2) Reactions, gaseous or otherwise, at the molecular level, leading to the formation of particles by condensation or sublimation of vapours with subsequent growth aided by

mutual coagulation of the small nuclei.

The first mechanism is generally responsible for the formation of the large nuclei, while the second mechanism leads to the formation of the smaller nuclei, generally called Aitken nuclei, with radii between 1.10^{-7} cm. and 2.10^{-5} cm.

The following sources are given by H. Landsberg[7] as the main natural sources of condensation nuclei: volcanic eruptions, radioactive radiation, evaporation and spraying of ocean water, soil dust, bacteria, pollen, ions from lightning, forest fires. To these we must add the nuclei produced directly or indirectly by human activity: nuclei are formed in combustion processes - domestic fires, industries, internal combustion engines, etc. Fletcher[8] discusses the possibility of condensation nucleus formation, as a result of sunlight causing photochemical reactions involving atmospheric trace gases. The ultraviolet radiation of the sun leads to the formation of oxides of nitrogen and ozone in the upper atmosphere, and lightning discharges produce the same trace gases in the lower atmosphere. The surface of the earth yields large quantities of many gases. Ammonia and hydrogen sulphide are liberated during the decay of animal or vegetable matter, while live animals release carbon dioxide. Plants, especially at warm temperatures, release volatile organic vapours such as terpenes, and hydrocarbons of many kinds are liberated in swamps and marshes.

Human activity such as domestic fires, motor cars, and industries contribute numerous trace gases to the atmosphere. The chief amongst these are sulphur dioxide, carbon dioxide, carbon monoxide, oxides of nitrogen, and hydrocarbons from

motor-car crankcases and exhausts.

In the following pages, we will examine some of the reports of research carried out by various workers on the formation of condensation nuclei by sunlight or artificial ultraviolet radiation.

A REVIEW OF LITERATURE ON THE FORMATION OF CONDENSATION NUCLEI BY SUNLIGHT AND BY ULTRAVIOLET RADIATION.

Aitken in 1897[9,10], measured abnormally high concentrations of condensation nuclei, when the sun was shining, at Kingairloch, a remote coastal village of West Scotland. He traced the source of these nuclei to the action of sunlight on the drying foreshore. He found that the concentration of nuclei increased with both the duration and intensity of sunlight. Aitken[11] investigated a similar effect in Falkirk, a town in fairly densely populated central Scotland, between 1909 and 1912. He observed that fogs were formed after sunrise, especially in winter, if the air had come from densely populated parts of the country, such as nearby Edinburgh, when the wind speed was less than about 3 miles per hour, and when the humidity was high. He ascertained that the formation of these so-called "sun-fogs" was not due to a change in the air temperature. The effect was much stronger with clear sunshine, than with sunshine through clouds.

During the automatic registration of atmospheric condensation nuclei, every fifteen minutes, at an altitude of 1800 m., over snow, in January and February in 1954, Verzar[12] noticed on sunny days, a regular increase of the nucleus count until midday, and a decrease in the afternoon. Since 2 meters of snow lay over

the country, it was improbable that the nuclei rose from the earth on warming by the sun, an explanation often given for this effect. The place of measurement was far away from human sources of pollution.

McLaughlin[13], reported a similar effect in Paris in 1926. Went[4] discussed the formation of blue or summer haze, over vegetation, far from sources of artificial pollution. He stated that these hazes are most prominent on quiet, sunny, summer days, with low wind velocities. He suggested that the hazes are produced as a result of photochemical reactions involving volatile organic vapours such as terpenes, emanating from vegetation.

Aitken[10, 11], investigated the formation of condensation nuclei in air and in various mixtures of gases, on irradiation with sunlight. He found that sulphur dioxide and pure air, in a silica flask which transmitted the short-wave radiation of sunlight, formed hygroscopic nuclei in sunlight. Sulphur dioxide and impure town air, in a similar experiment, formed a larger number of these nuclei. The diluted, filtered, gaseous products of a coal fire produced very large numbers of nuclei, on irradiation with sunlight. Aitken ascribed the production of nuclei in town air to a reaction between sulphur dioxide and some other impurity found in town air - not carbon dioxide or ammonia. Ammonia formed nuclei with sulphur dioxide in the dark. He suspected, as possible reaction partners for sulphur dioxide, the gases ozone, hydrogen peroxide and carbon monoxide.

Tyndall[14] as far back as 1870, showed that short-wavelength

light produced dense clouds within a tube containing air mixed with amyl-nitrite or certain other vapours.

Lenard and Wolff in 1889[15], and C.T.R. Wilson in 1898[16], noticed the formation of a very dense cloud on adiabatic expansion, in moist air in a glass/quartz container, when irradiated with ultraviolet light from a spark between zinc terminals, produced by an induction coil. C.T.R. Wilson showed that the nuclei thus produced were hygroscopic, and grew without any adiabatic expansion being made, when the air was irradiated for a long time, and the humidity was high. He showed that the nuclei were not caused by irradiation of the glass or quartz of the air container. He was able to produce large numbers of nuclei by UV-irradiation of a mixture of oxygen and water vapour, and of carbon dioxide, but very few nuclei were produced by UV-irradiation of hydrogen. C.T.R. Wilson suspected that the nuclei were formed as a result of the photochemical formation of hydrogen peroxide from water vapour and oxygen. He also found that a large number of very small nuclei were formed in moist air, by sunlight transmitted through quartz.

Saltmarsh in 1915[17] could not detect any hydrogen peroxide in a cloud chamber, after the formation of nuclei by ultraviolet radiation. Crane and Halpern in 1939[18], and Farley in 1951[19], associated the nucleus formation, in a conventional cloud chamber, with the presence of atomic oxygen. Atkinson in 1955[20], found that impurities emanating from the rubber diaphragm in a conventional cloud chamber, was responsible for the formation of UV nuclei (we will, in future, call the nuclei produced by ultra-

violet radiation by this name, for convenience).

Evans and co-workers[21], using a high pressure cloud chamber, at about 30 atmospheres pressure, found that ultraviolet light of wavelength greater than 1800A always produced large numbers of nuclei in argon-water vapour, argon-oxygen-water vapour, nitrogen-water and nitrogen-oxygen-water vapour mixtures, while ultraviolet light of wavelength greater than 2500A produced no nuclei in these mixtures. With wavelength greater than 2200A, the nucleus production varied from gas mixture to gas mixture in a complicated manner. After irradiation of a nitrogen-oxygen-water vapour mixture, with UV wavelength greater than 2200A, a chemical test for nitrogen dioxide was very positive.

Barnard and Mouton in 1958[22], were only able to produce very few nuclei in an ultra-clean glass/quartz chamber, with purified air and water vapour. McHenry and Twomey in 1952[23], found the effective wavelength for UV nucleus production, to lie between 2345A and 2399A. They found a great increase in UV nucleus production when they added ammonia to moist air, the increase in nucleus production being proportional to the ammonia concentration, which ranged from 0.57 to 1.14 mm. Hg. They were able to form large numbers of nuclei by irradiating cylinder nitrogen, but found no such production with cylinder oxygen.

Verzar et al., 1957, 1959[24, 12], found that large numbers of nuclei were produced by sunlight, in filtered atmospheric air, cylinder nitrogen and oxygen, in a polyethylene balloon, and that great increases in UV nucleus production took place when small amounts of hydrogen sulphide, sulphur dioxide, and relatively

large amounts of ammonia were added to the air in the balloon. However McGreevy and O'Connor, 1962[25], and the author[26], showed that polyethylene itself was a prolific source of nuclei on irradiation with sunlight, or ultraviolet light, so that any nuclei produced by sunlight in the gases in the polyethylene balloon, would be masked by the nuclei produced by the balloon itself.

Vassail in 1949[27], reported that large ions were formed in air, oxygen, carbon dioxide and hydrogen. He suggested that simple hygroscopic molecules, photochemically formed, such as hydrogen peroxide or nitric acid, might act as condensation nuclei. Evans and Watson 1965[28], found strong evidence that the nuclei created by an electric field in a nitrogen-water vapour mixture, were due to the formation of nitrous and nitric acids. Vassail found that radiation in the region 1800A to 1850A was most effective in producing nuclei. Addition of sulphur dioxide, carbon tetrachloride, carbon disulphide, and relatively large amounts of hydrogen sulphide, caused a great increase in the number of nuclei produced. Gas dried by sulphuric acid or phosphoric acid formed very few UV nuclei.

Mulcahy and Kuffel in 1962[29], got similar rates of nucleus production on UV irradiation of moist air or moist Argon. The concentration of nuclei produced increased with increasing humidity of these gases, and no nuclei were produced in dry air or dry Argon. They showed, as did Saltmarsh that the nuclei were largely electrically uncharged. They found the most effective wavelength for nucleus production to be below 2400A. They

supported Wilson's hypothesis that the nuclei consisted of hydrogen peroxide.

Dunham (1961)[30], was able to produce very large numbers of nuclei by irradiating a mixture of sulphur dioxide and air, with UV radiation.

In a series of experiments, Walter Hoppe[31], using an automatic Pollak nucleus counter, managed to produce a large number of UV nuclei in cylinder oxygen and nitrogen, a much smaller number in Argon, and none at all in hydrogen. He found convincing evidence that the formation of UV nuclei in atmospheric air was due to the presence of a trace gas, that reacted photochemically, and was gradually consumed, on prolonged irradiation. He added definite quantities of ammonia, hydrogen sulphide and sulphur dioxide to the atmospheric air which he irradiated. He claimed that the atmospheric concentration of hydrogen sulphide or ammonia was not sufficiently high to explain the UV effect in air, whereas the atmospheric concentration of sulphur dioxide was of the right order of magnitude. His conclusion that sulphur dioxide takes part in the formation of the UV nuclei was supported by the fact that sulphur dioxide concentration in the atmosphere, and the UV effect, showed similar diurnal variations.

In 1950, Dainton and Ivin[32], reported a mist-forming photochemical reaction between sulphur dioxide and hydrocarbons - which are emitted from motor-car crankcases and exhausts. In 1958, Schuck, Ford and Stephens[33] reported that the addition of sulphur dioxide to motor-car exhaust-air mixtures, led to dramatic

increases in the rate of nucleus formation, on irradiation with ultraviolet light. The following year, Doyle with Schuck[34], and Renzetti[35], reported a similar effect on irradiation of nitric oxide - nitrogen dioxide - olefin mixtures in air.

On the other hand, Renzetti and Doyle[35] found that the addition of small quantities of olefin hydrocarbons to photo-oxidizing sulphur dioxide, at a concentration of 0.3 ppm (part per million by volume) in air, at 50°/o relative humidity, had a strong suppressive effect on the production of nuclei. They also obtained some evidence that addition of 1 ppm nitric oxide hindered the formation of nuclei.

After examining these reports of various workers, over the past century, on the formation of condensation nuclei by sunlight or ultraviolet radiation in various gases, and mixtures of gases, one is left in a state of great confusion. Results of various workers often appear to be completely contradictory, as regards such points as what trace gas, if any, is responsible for nucleus production, what range of wavelength is most effective, whether UV nuclei are formed in permanent gases such as nitrogen, oxygen, argon, carbon dioxide or hydrogen.

Generally, there has been a great lack of standardization of experimental procedure, and experimental conditions such as the range and intensity of light used, the time of exposure, the material of the irradiation chamber, etc. The concentrations of trace gases used has often differed enormously from the concentrations normally found in the atmosphere. Other possible reasons for apparent contradiction between results of various workers

are discussed later on in this work. On the whole, it seems that the problem has been over-simplified, as various workers have assumed that one and only one trace gas in the atmosphere was responsible for UV nucleus production, whereas it now seems clear that many gases and mixtures of gases can form nuclei on irradiation with ultraviolet light.

In the author's work it was decided to investigate in detail the nucleus production in atmospheric air, using only the range of wavelength found in solar radiation in the lower atmosphere. It was thought that it would be of great interest to relate the results of this laboratory work to the serious problem of haze formation in artificially and naturally polluted air, by sunlight.

DESCRIPTION OF APPARATUS AND GENERAL EXPERIMENTAL PROCEDURE

The apparatus described here is that part of the apparatus that was common to the various sections of this work. The apparatus used in specific experiments will be described as necessary.

Irradiation chamber: In the present work the gas to be tested for production of condensation nuclei, on irradiation with ultraviolet light, was exposed to the ultraviolet light in a 6.5 litre cylindrical flask of borosilicate glass, of average thickness 6.1 mm. This flask had ground glass connections, so that all internal surfaces exposed to the UV radiation were of glass. Other workers, particularly McGreevy and O'Connor[25], and

O'Connor[36] found that many surfaces such as plexiglass, polyethylene, rubber, and cork, but not borosilicate glass were prolific producers of condensation nuclei on irradiation with sunlight, or ultraviolet light. The author[26] found that a similar borosilicate glass flask, after being washed thoroughly with hot water and teepol, gave rise to copious production of nuclei on irradiation with ultraviolet light. However, this nucleus production was of a transient nature, and decayed to zero when the flask had been exposed to the ultraviolet radiation for three hours. Subsequent exposures of the flask to ultraviolet light did not lead to any further nucleus production, although the flask had been continuously flushed with filtered town air.

Borosilicate glass strongly absorbs all ultraviolet radiation of wavelength less than about 2900A. The transmission characteristics of the glass in the flask are discussed in more detail later on in this work.

Ultraviolet lamp: The ultraviolet lamp used to irradiate the gas in the flask, was a Philips type MLU 300 watt lamp. This lamp consists of a high pressure quartz mercury discharge tube in series with a tungsten filament which acts as a ballast. The ballast is used to balance the negative volt ampere characteristic of the mercury arc. Both the mercury tube and the tungsten ballast are incorporated in a thin glass protecting bulb, with a mirror reflector at the rear. In a low pressure mercury arc, operated with alternating current of frequency 50 c/sec., the radiation from the tube follows the current through the tube very closely, falling to zero, a hundred times per second. In a high pressure

lamp, such as the MLU 300 watt, operated with alternating current of frequency 50 c/sec., the radiation from the lamp is also modulated at 100 c/sec., but does not actually fall to zero, when the current falls to zero. This is so, because, at the high temperature of the high pressure arc, the heat capacity of the arc is sufficient to cause appreciable thermal excitation of the gas. The radiation of the MLU 300 watt lamp is quite insensitive to ambient temperature changes, due to the poor conductivity of the double bulb arrangement.

The intensity of the UV radiation from the lamp varies approximately inversely as the square of the distance from the arc, along the main axis of the lamp. Fig. I shows the irradiation pattern of the lamp in a plane perpendicular to the main axis of the lamp, at a distance of 50 cm. from the front of the lamp. The arc itself is approximately 8 cm. behind the glass front of the lamp. Fig. I shows a curve relating the intensity at points on this plane, to their distance from the main axis of the lamp, along the plane. This curve was supplied by the manufacturers of the lamp. In all the experiments described in this work, a standard distance of lamp to flask was used, this being 15.7 cm. from the front of the lamp to the nearest wall of the flask - see Fig. 2. The lamp was also always placed in such a way that its main axis bisects the main (vertical) axis of the flask. The flask was placed in a wooden container, with a blackened interior, and one side left open (to allow for cooling), so that the gas in the flask was subject to minimum irradiation from sources other than the one UV lamp. There are suitable holes bored in the roof

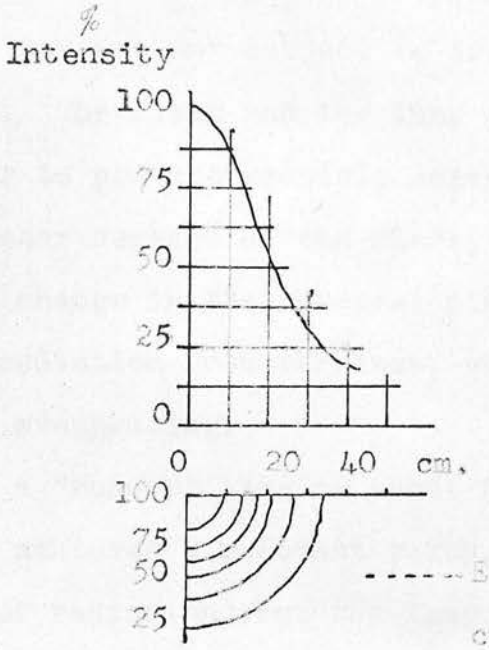


Figure 1:

The irradiation pattern of the MLU 300W UV Lamp.

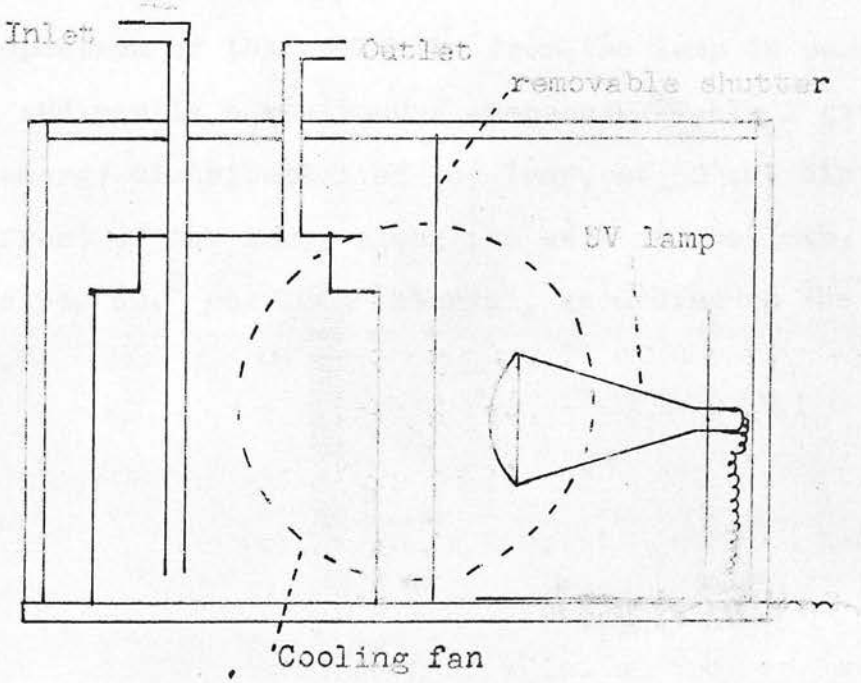


Figure 2: The arrangement of the flask and lamp.

of the wooden container, through which connections to the flask are led, so that they are not subject to irradiation from the UV lamp (see Fig. 2). The flask and the lamp are cooled by a ten inch fan, in order to prevent possible emission of condensation nuclei from the inner surface of the flask, due to heating, and also to prevent a change in the spectral distribution and total energy of the UV radiation from the lamp, which has been found to occur on gross overheating.

The lamp has a "run-up" time of about 2 minutes, before the radiation from it achieves a constant value. The depreciation in the intensity of radiation from the lamp is dependent on the number of times the lamp has been switched on. For these two reasons, an exposure of the gas in the flask, to the radiation of the lamp was generally commenced by removing an opaque shutter from between the lamp and the flask.

The spectrum of the radiation from the lamp is partly a line spectrum, and partly a continuous spectrum. Table I gives the spectral energy distribution of the lamp, at 50 cm. distance from the front of the lamp, along the axis of the lamp, in microwatts per $cm.^2$ per 100A interval, according to the manufacturers.

TABLE I

The spectral energy distribution of UV lamp MLU 300 watts in $\mu W/cm^2/100A$ at 50 cm. from lamp.

Line spectrum		Continuous spectrum	
λ	$\mu W/cm^2/100A$	λ	$\mu W/cm^2/100A$
2804	10.0	2750	10.0
2894	10.0	2850	20.0
2967	60.0	2950	30.0
3025	170.0	3050	40.0
3130	530.0	3150	50.0
3341	70.0	3250	50.0
3655	1330.0	3350	50.0
4047	420.0	3450	40.0
4358	780.0	3550	30.0
5461	970.0	3650	30.0
5780	950.0	3750	20.0
		3850	20.0
		3950	10.0
		4050	10.0

The counting of nuclei: For the purpose of measuring the concentration of condensation nuclei in the gas from the flask, a Nolan-Pollak photoelectric nucleus counter was used. The counter and its operation, is described by Metnieks and Pollak[37]. Most of the counter used in this work, was built under the direction of the author.

A schematic diagram of the counter is shown in Fig. 3. The counter basically consists of a vertical brass tube of length 58.7 cm., which is sealed at both ends by glass plates, using O-ring sealing, to make the joints leakproof. The glass plates are coated, on the inside, with a conducting layer, and can be slightly heated electrically in order to prevent condensation on them. A 6 volt accumulator was used to provide the heating currents, which were measured by two milliammeters, the two glasses being connected in parallel. For convenience, the heated glasses circuit is not shown in Fig. 3.

The counter is fitted with four vacuum taps, one at both ends of the brass tube, and two symmetrically arranged at the centre of the tube. The brass tube, commonly called the fog-tube, is lined with moist porous ceramic of internal diameter 2.5 cm. The lamp house, on top of the fog-tube, produces a parallel beam of light, of diameter less than that of the fog-tube, which strikes a photoelectric selenium cell, which is under the lower heated glass. The photoelectric current is measured by a Sangamo-Weston model S-82 microammeter, with range 0-15 microamps, critically damped by a parallel resistance of 55,000 ohms. The light bulb in the lamp house is fed by a 6-volt, large capacity

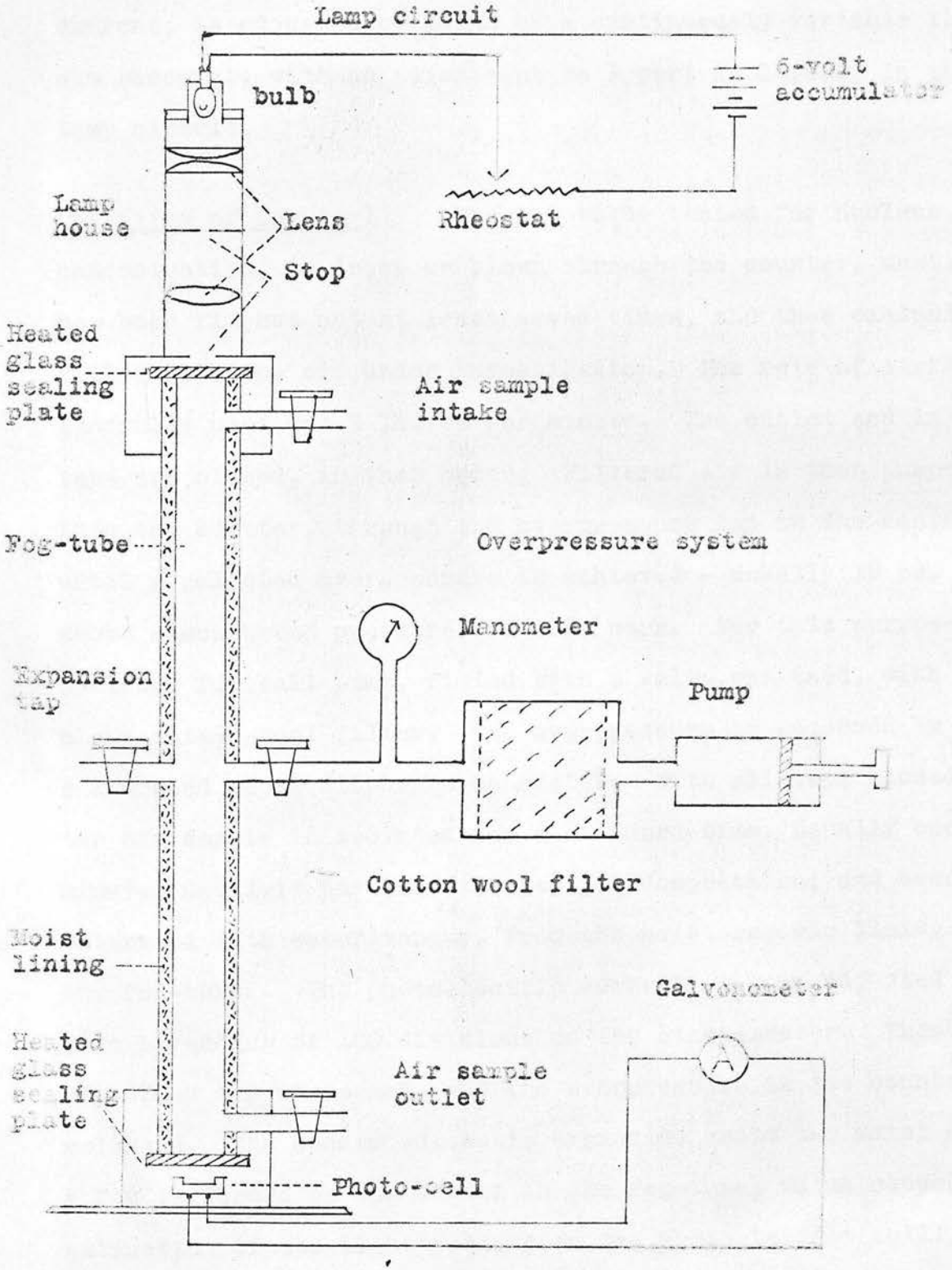


Figure 3 : Schematic diagram of photo-electric counter.

accumulator. The light intensity, and hence the photoelectric current, is adjusted by means of a continuously variable 1.25 ohm rheostat, with an adjustment to 1 part in 10,000, in the lamp circuit.

Operation of Counter: The gas to be tested for nucleus concentration, is drawn or blown through the counter, until it has been flushed out at least seven times, and thus exclusively filled with the air under investigation. The rate of airflow generally used was 3 litres per minute. The outlet and inlet taps are closed, in that order. Filtered air is then pumped into the counter, through the overpressure tap in the centre, until a selected overpressure is achieved - usually 16 cm. Hg. above atmospheric pressure, in this work. For this purpose an ordinary football pump, fitted with a valve was used, with a clean cotton-wool filter. The overpressure is measured by a calibrated metal diaphragm manometer. With all taps closed, the air sample is isolated for a standard time, usually one minute, until it has lost the heat of compression, and become saturated with water vapour, from the moist ceramic lining of the fog-tube. The photoelectric current i_o is adjusted to give a reading of 100 divisions on the microammeter. Then the expansion tap is opened, and the overpressure in the counter released. The sudden adiabatic expansion cools the moist air, a fog is formed on the nuclei in the fog-tube, which causes an extinction of the light falling on the photoelectric cell. The photoelectric current and hence the galvanometer reading fall to new values, i and R respectively. $R = 100(i/i_o)$. and

the extinction $E = 100(i_o - i)/i_o$. The relationship between the extinction E and the concentration of nuclei has been determined experimentally by Nolan and Pollak, 1946[38], who established one count by comparison with an Aitken absolute dust counter[39] and obtained a complete calibration curve by successive dilution of a standard aerosol stored in a large gasometer. More recently, Pollak and Metnieks 1959[40], prepared new calibration tables, with the aid of a stereo-photomicrographic recording absolute nucleus counter (Pollak and Daly, 1958[41]. These 1959 tables relating the reading R and extinction E to nucleus concentration, for standard conditions of operation of the nucleus counter, were used in this work. It must be stressed that the nucleus counter was used in this work to measure relative concentrations of nuclei, rather than absolute concentrations, as the average accuracy of the counter for absolute measurements of various distributions of nuclei, is not better than 10°/o of the nucleus concentration.

Theory: The theory of the extinction of a parallel light beam by a fog, is very complex. The transmission of a parallel light beam, through a fog of water drops is, according to Metnieks and Pollak[37],

$$I/I_o = \exp(-\pi z \leq nr^2 K) \qquad (1)$$

where I_o is the flux density of the incident parallel beam, I the flux density of the parallel beam after passing a distance z through the fog, n the number of spheres of radius r, per unit volume, and K the appropriate total Mie scattering area

coefficient, which only applies strictly to a very low concentration of droplets. K is a dimensionless coefficient, and depends on the index of refraction (1.33 in our case) of the droplets, against the dispersion medium, and a parameter $a = 2\pi r/\lambda$, r being the radius of the fog droplets and λ the wavelength of the light. Penndorf, 1956[42], has prepared extensive tables for K, for various values of a, and the index of refraction.

The summation in equation (1) has to be taken over all sizes of droplets present. Equation (1) takes no account of coherence in the scattering of a large number of droplets, and it does not allow for multiple scattering. Equation (1) holds for one single wavelength only, and must be integrated over the range of wavelengths present in non-monochromatic light. It is obvious therefore, that it would be an extremely difficult problem to produce a theoretical calibration curve for the Nolan-Pollak counter, and this is why a largely empirical calibration has been used.

Maintenance of Counter: The ceramic lining of the counter was regularly watered with de-ionized water, in accordance with the instructions for use of the counters. After each watering, the light beam was carefully centered in the fog-tube. In order to do this, the photo-cell was removed, and looking through the lower heated glass, the lamp-house screws, which were spring loaded, were adjusted, if necessary, to give a central light beam. The counter taps were regularly deaned, and greased with apiezon grease. The electric currents through both heated glasses, at

the recommended values of 70 mA for the upper glass and 150 mA for the lower glass, were regularly checked, as the electrical contacts to the heated glasses occasionally gave trouble.

Measurement of the rate of gas-flow: The rate of gas-flow, which could be varied from 0.5 to 20.0 litres per minute, was measured by one of a set of three Rotameter type flowmeters. These flowmeters had been calibrated by the manufacturers, for rates of flow of air, at a temperature of 15°C, and 760 mm. Hg pressure. The accuracy claimed for these rotameters is ± 2% of indicated flow. A drying tube, containing silica gel, was normally placed in the gas line, just before the rotameter, in order to prevent condensation of water vapour in the rotameter. The gas-flow was provided by a rotary vacuum pump. A very large cotton-wool filter was placed in the gas line, before the vacuum pump, in order to damp out fluctuations in the rate of gas flow. The gas was normally drawn through the borosilicate flask and counter, and the apparatus was regularly tested for leakages. The rate of gas flow was regulated by adjusting bleeds, throttles and Hoffman clips, placed at convenient points in the apparatus.

Gas filters: The cotton-wool filters used to filter atmospheric nuclei from the air, were made in accordance with the instructions for use of the counters. Fresh, clean cotton wool was always used in making these filters.

Also used were Millipore cellulose filters. These are thin porous structures composed of pure inert cellulose esters. Pore sizes are extraordinarily uniform in size. Two grades,

with pore sizes 0.22 micron and 1.2 micron respectively were used at various s tages of this work. In gas filtration, because of the enormous specific surface and high resistivity of the Millipore filter, substantial electrostatic charges are generated and held. This negative charge prevents the passage of particles far smaller in dimension than the filter pore size. The filters used in this work were of 47 mm. diameter and were mounted in either a Millipore stainless steel leakproof holder or in an aluminium holder.

UV IRRADIATION OF FILTERED ATMOSPHERIC AIR, USING THE STATIC METHOD

In this work two main methods have been used to expose air in the flask to the ultraviolet radiation. The first method, described hereunder, is called the static method, because the air which had been filtered effectively by means of a cotton wool filter, removing all atmospheric condensation nuclei, was isolated in the flask, while it was exposed to the ultraviolet radiation.

Arrangement of apparatus:

Fig. 4 shows the schematic arrangement of apparatus, for this method. Outdoor air was drawn into the flask, through a cotton wool filter, from a tube which passed through a hole in the frame of a closed laboratory window. This inlet tube was at a height of twelve feet above ground level, outside the window. The air, after filtration, entered the flask through a long borosilicate glass tube, with its exit inside the flask, at the bottom. The air left the flask through an opening at the top of the flask, passing through

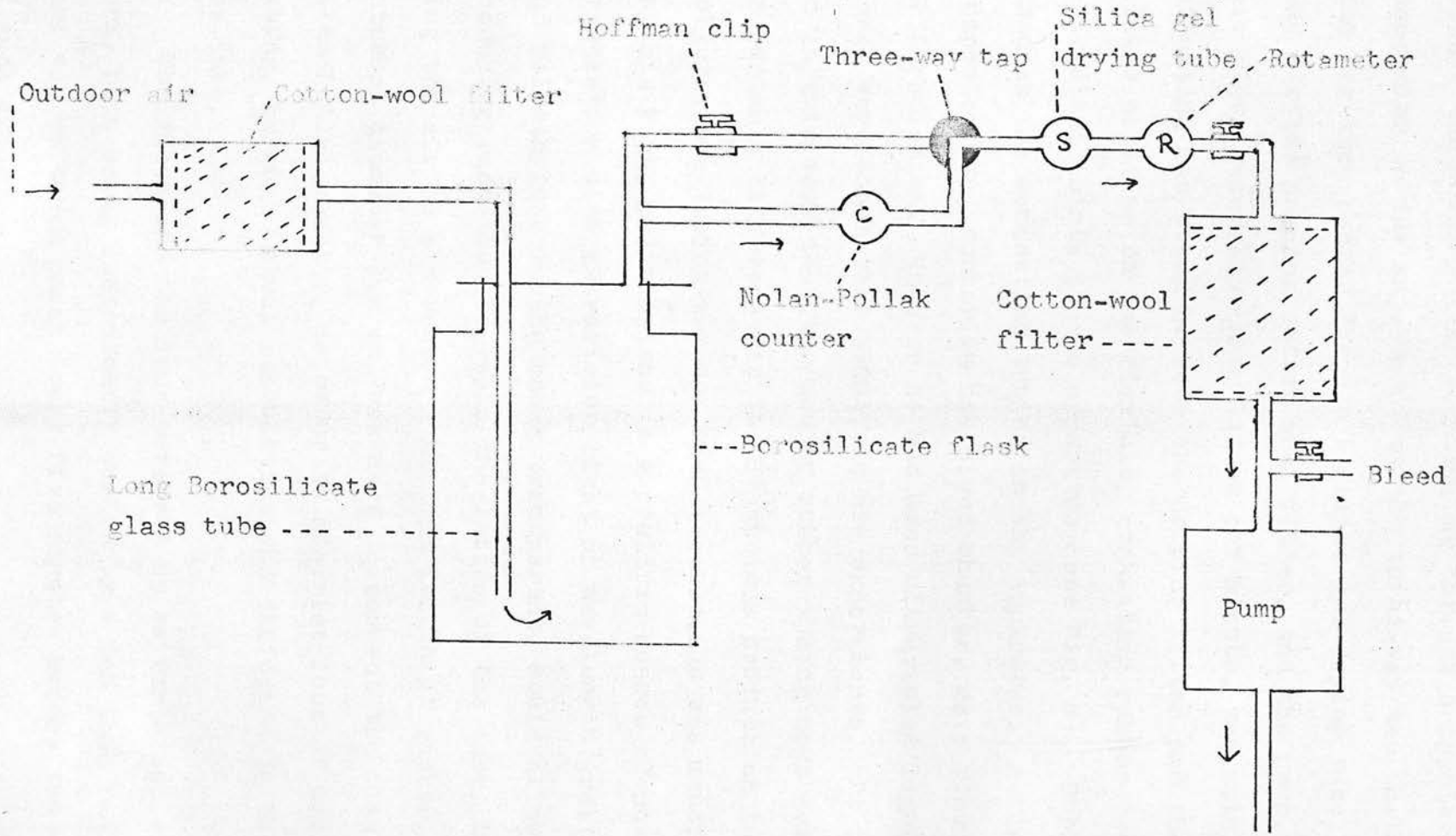


Figure 4 : The schematic arrangement of apparatus for the static and dynamic methods of irradiation. Arrows show direction of airflow.

either the Nolan-Pollak counter, or through a counter bypass tube, depending on the adjustment of the three-way tap in the air line. The air then passed through a silica gel drying tube, a Rotameter, the airflow damping cotton wool filter, and the pump. The rate of air flow, generally three litres per minute, was maintained by adjusting the bleed between the damping filter and the pump, and clamps or clips on the flexible, connecting rubber tubing at convenient points in the apparatus (see Fig. 4). Rubber tubing was used as the connecting tubing in the apparatus. Atkinson[20] suspected that rubber in his cloud chamber, gave rise to nuclei on UV irradiation. However he had used ultraviolet light of much lower wavelength than 2900A, in his experiments. It is shown later on in this work that the use of rubber tubing does not make an appreciable difference to the UV nucleus production in the flask. Polyethylene tubing was not used because, as was mentioned earlier in this work, polyethylene is a prolific source of nuclei on irradiation with ultraviolet light of wavelength greater than 2900A, and polyethylene tubing being transparent, would allow the nucleus producing radiation to reach the inside of the tube, thus contaminating the air in the tube. A minimum length of rubber tubing, of internal diameter 1.2 cm. was used to connect the flask and the Nolan-Pollak counter, in order to minimise loss of nuclei in the tubing, through mutual coagulation and diffusion to the walls of the tube.

The flask and the lamp were set up as explained earlier in this work, both being continuously cooled by a ten inch fan. The UV lamp was switched on at least five minutes before the commencement of each exposure.

Experimental Procedure:

The flask was normally flushed before each irradiation, with at least ten times its volume of the filtered air under investigation, so that a completely fresh sample of air was irradiated. A test measurement of nucleus concentration was made two minutes before each exposure, in order to ensure that the air in the flask was properly filtered, and that there were no leaks in the apparatus. The airflow was stopped one minute before the exposure, by switching off the pump. The flask inlet and outlet tubes were then clamped shut, with clips, near the flask, so that the air sample was isolated in the flask.

The exposure to the ultraviolet radiation was now commenced, by removing the shutter between the UV lamp and the flask.

The flask was now irradiated for the desired exposure time, and the irradiation was stopped by replacing the shutter between the lamp and the flask. The clips on the inlet and outlet tubing to the flask, were quickly re-opened, and the pump was switched on again 15 seconds after the end of the irradiation. The irradiated air from the flask, at a flow rate of three litres per minute, was drawn through the Nolan-Pollak counter. One minute after the end of the irradiation, a sample of this air was isolated in the counter by first of all diverting the airflow through the counter bypass tube, by means of the three-way tap, and then immediately closing the counter outlet and inlet taps. A measurement of the nucleus concentration in this isolated air was made as explained on page 19, using the standard waiting time and overpressure of one minute and 160 mm. Hg respectively. The nucleus concentration thus recorded, was probably not exactly the

same as that in the flask after irradiation due to the fact that fresh filtered air coming into the flask, admittedly at the bottom, would have diluted to some extent the original nucleus concentration in the flask. However, some dilution had to be suffered, otherwise the nucleus counter would not be flushed with a sufficient volume of the irradiated air, to give a representative measurement of nucleus concentration. Thus the time (45 secs.) allowed to lapse between the re-commencement of the airflow, after the irradiation, and the isolation of the irradiated air sample in the counter was a compromise. Some loss of nuclei also occurred before measurement, due to mutual coagulation and diffusion, to the walls of the apparatus. However, as the same standard experimental procedure was used in all static exposures, it was possible to get quite reliable relative measurements of nucleus concentration.

Dependence of Concentration of UV Nuclei Produced, on Irradiation Time, in the Static Method.

The static method of irradiation was now used, with various irradiation times, ranging from 0.5 minute to 30.0 minutes. All the experiments were carried out over a period of three consecutive days. For each experiment, the flask was flushed with the outdoor air, which had been filtered through a cotton wool filter, for a standard time of 22.0 minutes. The exact experimental procedure used, is given below. T is the time after the commencement of the experiment, in minutes, and E is the irradiation or exposure time.

T (minutes)	
0.0	Last measurement of nucleus concentration, if any, was made.
15.0	The airflow was diverted from the counter bypass tube to the counter.
16.0	An air sample was isolated in the counter.
17.0	A test measurement of the nucleus concentration in the filtered air was made.
17.75	The pump was switched off, and the counter taps were closed, isolating the air in the flask.
18.0	The irradiation of the air in the flask was commenced.
18.0 + E	The irradiation of the air was stopped, by replacing the shutter between the UV lamp and the flask.
18.0 + E + 0.25	The counter taps were opened. The pump was restarted, drawing irradiated air from the flask through the counter.
18.0 + E + 1.0	An irradiated air sample was isolated in the counter.
18.0 + E + 2.0	A counter expansion was made, giving a measurement of nucleus concentration Z.
18.0 + E + 4.0	The stopwatch hands were put back to zero, and the next experiment commenced.

Fig. 5 shows the results of this series of experiments, as a plot of UV nucleus concentration Z against the exposure time E. Z increased very rapidly with exposure time, after the first minute, reaching a maximum value of 278,000 per c.c. at 6.0 minutes exposure time. Thereafter Z decreased slowly with exposure time, reaching a value of 163,000 per c.c. or approximately 60°/o of the maximum concentration after 30.0 minutes

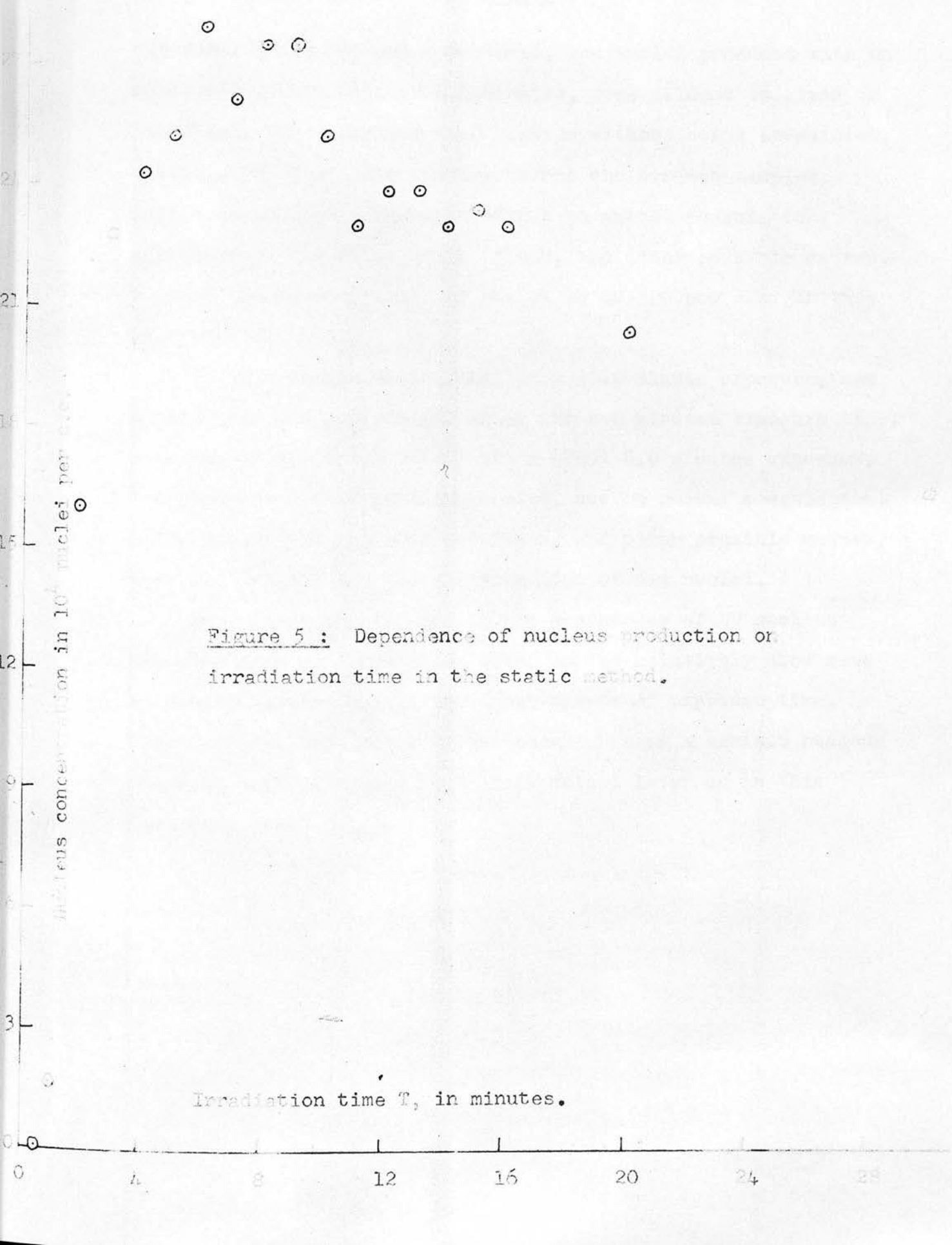


Figure 5 : Dependence of nucleus production on irradiation time in the static method.

exposure. In a control experiment, the nuclei produced with an optimum exposure time of 6.0 minutes, were allowed to stand in the flask, for a further 24.0 minutes without being irradiated, making a total of 30.0 minutes before the air was sampled. Losses in nucleus concentration due to mutual coagulation, diffusion to the walls of the flask, and other possible causes, reduced the concentration of nuclei to 42,300 per c.c. in this 24.0 minutes.

It thus seemed clear, that in a 30.0 minute exposure, new nuclei were being produced, after the 6.0 minutes exposure time, although at a reduced rate. After about 6.0 minutes exposure, the rate of loss of existing nuclei, due to mutual coagulation, diffusion to the walls of the flask, and other possible causes, was greater than the rate of formation of new nuclei.

An interesting feature of the dependence of UV nucleus concentration on irradiation time, is the relatively slow rate of nucleus production in the first minute of exposure time. This feature, together with the occurrence of a maximum nucleus concentration is discussed in more detail later on in this work (see page 36).

UV IRRADIATION OF FILTERED ATMOSPHERIC AIR, USING THE DYNAMIC METHOD

The second method used for irradiating the air, is called the dynamic method, because the air was circulated through the flask at rates of flow, which could be varied from 0.5 to 20.0 litres per minute, while the air passing through the flask was irradiated by the ultraviolet light. The exact same arrangement of apparatus was used, as for the static method. The air after irradiation in the flask, passed through either the photoelectric counter or the counter bypass tube. The rate of airflow was maintained at the same value whether the air passed through the counter, or through the bypass tube, by adjusting a Hoffman clip.

Dependence of Concentration of UV Nuclei Produced, on Irradiation Time, in the Dynamic Method

One of the main experiments carried out, using the dynamic method, was an experiment designed to investigate the dependence of UV nucleus production, in filtered air passing through the flask, at a specified flow rate, on the time of irradiation.

Experimental Procedure:

The flask was flushed with filtered air, at the same air flow as it was proposed to use during irradiation, for a sufficiently long time to pass at least ten times its volume of filtered air through it. The rate of airflow normally used was 3.0 litres per minute, and the corresponding flushing time was 22.0 minutes. As in the static method, a test measurement of nucleus concentration in the filtered air was made two minutes before the

commencement of irradiation, in order to check that the air was being effectively filtered. The irradiation of the air in the flask was commenced, as usual, by removing the shutter between the lamp and the flask. With the normal airflow rate of 3.0 litres per minute, nucleus concentrations were measured every two minutes. The first minute was allowed for the flushing and filling of the counter with a completely fresh sample of irradiated air. The other minute was the standard waiting time between the isolation of the air sample in the counter, and the making of the expansion. The switch-over of the air current from the counter to the counter bypass tube, was always speedily accomplished, so as to minimise any disturbance caused to the rate of airflow through the flask.

Results: In the dynamic method of irradiation, a consistent pattern of production was observed. The concentration of UV nuclei increased rapidly with time of exposure, after the first minute, reaching a maximum concentration, as in the static method. This maximum concentration occurred with remarkable consistency five to seven minutes after commencing the UV irradiation of the flask. There were only one or two exceptions in a total of about thirty experiments, where the maximum concentration occurred at some other time. After reaching the maximum, the nucleus concentration decreased gradually with time, reaching a value after 30 to 40 minutes, which remained approximately constant for at least 2.5 hours more, when outdoor air which had been filtered through cotton wool was used. This "steady-state" nucleus concentration generally fluctuated by, at most, about 12% of its

mean value, in a random fashion, but showed no tendency to increase or decrease.

Fig. 6 is a typical plot of UV nucleus concentration Z against the time T measured from the commencement of irradiation. A particular nucleus concentration Z, is taken as corresponding to the time when the air sample containing those nuclei was isolated in the nucleus counter, and not the time of the expansion, one minute later. The airflow rate for this experiment was 3.0 litres per minute. This airflow rate gives an average residence time, for the air in the flask, of 2 minutes ten seconds. Due to mixing in the flask, however, some of the air will be exposed for a longer period than this, and some for shorter periods. The air used for this experiment was outdoor air, filtered through a cotton wool filter. Maximum nucleus concentration, at 144,000 per c.c. of air, occurred 7 minutes after the commencement of the irradiation. The steady state nucleus concentration was about 40,000 per c.c. or approximately 28% of the maximum concentration.

When the air used was outdoor air which had been filtered through a cotton wool filter, the maximum nucleus concentration reached in experiments on various days, at an airflow rate of 3.0 litres per minute, did not vary by more than about 15% of the mean maximum concentration, from day to day. Some experiments were carried out, in which the flask was flushed out beforehand for longer and shorter periods than the normal 22.0 minutes. Table 2 shows the flushing time, the maximum concentration Z_{max} and the minimum concentration of nuclei Z_{min} recorded in 1 hour long experiments.

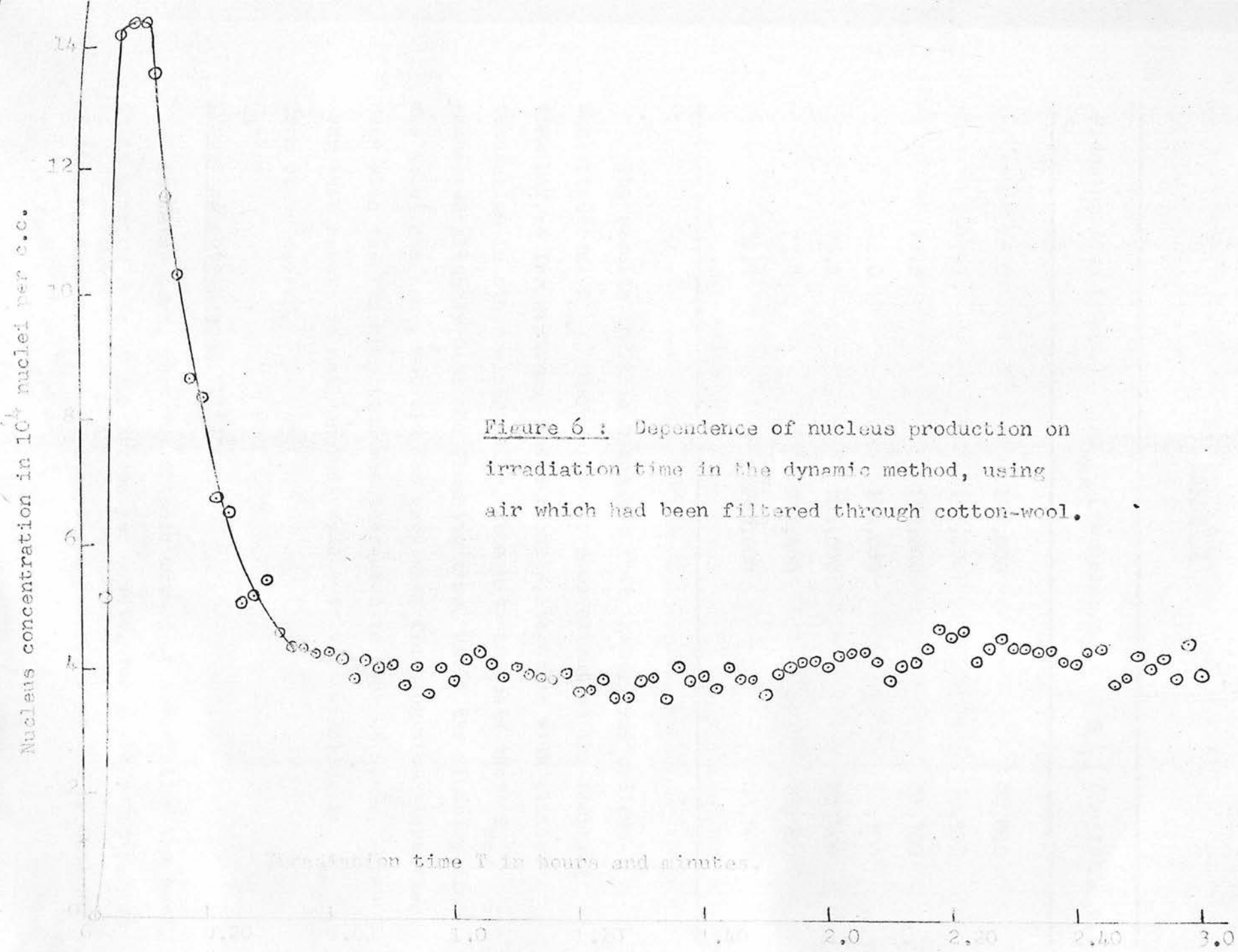


Figure 6 : Dependence of nucleus production on irradiation time in the dynamic method, using air which had been filtered through cotton-wool.

TABLE 2

Flushing time (mins.)	Z_{max} (nuclei/c.c.)	Z_{min} (nuclei/c.c.)
16.0	116,000	47,000
17.0	173,000	33,300
19.0	182,000	31,700
22.0	144,000	36,100
75.0	201,000	40,400
77.0	211,000	66,700
130.0	206,000	43,800

The results in Table 2 suggest that the maximum nucleus concentration Z_{max}, may depend to some extent on the flushing time before irradiation. These results, together with similar tendencies in other experiments, seemed to indicate that Z_{max} increased slightly with the flushing time, until the flushing time was about one hour, but did not vary with flushing time thereafter, even when the flushing time was increased to over 48 hours. However this result is not conclusive, due to the variation in Z_{max} from other causes.

Effect of cotton-wool filter:

In later work, when the dynamic method of irradiation was used, at an airflow rate of 3.0 litres per minute, for a prolonged period of time (a few weeks), some unexpected behaviour of the UV nucleus

production was observed. On some days the steady-state nucleus production dropped to zero, and in general the rate of nucleus production varied much more than usual, from day to day. It was now suspected that the filter, when used normally for about three out of 24 hours, was in some way damping out day to day fluctuations in the concentration of some trace gas or vapour in the air, responsible for UV nucleus formation. This damping would probably be caused by absorption and desorption of the trace gas X in the cotton wool. Thus, if there was a high concentration of X in the air coming into the filter, the cotton wool would absorb some of X, until the cotton wool was saturated with X, with the result that the concentration of X in the air would normally be reduced. On the other hand, if the concentration of X in the incoming air was lower than average, some of the X already absorbed, in the cotton wool, perhaps from a previous day, would be desorbed into the air stream, thus increasing the concentration of X in the air. On prolonged use of the filter, the changes in the concentration of X in the air passing through the filter would be more gradual, than if the filter were only used for a few hours every day. A filter used for a few hours every day would then have a more pronounced damping effect on the concentration of X in the air, than a filter in prolonged, continuous use.

It was later discovered that Aitken[11], had noticed that "a filter (cotton wool) through which strong products have been passed is difficult to cleanse by pumping air through it..." He also suggested that "Part of the persistency in the condensation, would no doubt be due to some of the gases absorbed at first by the filter, getting free when pure air was passing."

It is also possible that absorption of other substances such as water, by the cotton wool filter would alter the concentration of X in the air passing through it.

On one of the days that the UV nucleus concentration, in a prolonged dynamic experiment had dropped to zero, the air after passing through the cotton wool filter was tested for sulphur dioxide concentration. The sulphur dioxide test is described later on in this work. No sulphur dioxide was detected, although a control measurement showed that the sulphur dioxide concentration in the unfiltered air was 2.5 pphm, (part per hundred million, by volume), lower than the daytime average at that time of the year.

As a result of the above observations, it was decided to use Millipore filters in all future experiments. These had not been used previously, because it had been found that using outdoor air at an airflow of 3.0 litres per minute, a Millipore filter of pore size 1.2 micron occasionally allowed up to 2,000 nuclei per c.c. through. A 0.22 micron pore size Millipore filter was always much more efficient. However the use of this filter had the serious disadvantage that a considerable pressure drop occurred across the filter. This greatly increased the risk of leakage in the apparatus. There was also the undesirable effect that when the airflow was interrupted, (i.e. when altering the setting of the three-way tap), that an expansion of the gas in the flask resulted at times.

The use of a 1.2 micron pore size Millipore filter, at an airflow rate of 1.0 litres per minute resulted in efficient filtration, but the UV nucleus concentrations reached in the

in the dynamic experiment were sometimes greater than 270,000 per c.c. and too high to be measured with even reasonable accuracy by the Nolan-Pollak counter. According to the calibration tables, an extinction of 93.9% after expansion in the counter, corresponds to 269,290 nuclei/c.c.

Results of the Dynamic Experiment, on using a Millipore Filter:

The pattern of nucleus production was similar to the pattern of nucleus production on using a cotton wool filter, except that

(1) The maximum UV nucleus concentration, and the mean steady-state UV nucleus concentration varied more from day to day.

(2) The final steady-state UV nucleus concentration reached, was not at all as steady or as constant as with air which had been filtered through a cotton wool filter.

(3) The steady-state UV nucleus concentration was generally a smaller fraction of the maximum concentration, than with air which had been filtered through a cotton wool filter.

Fig. 7 shows the results of an hour long dynamic experiment, at an airflow rate of 3.0 litres per minute, using a 0.22 micron pore size Millipore filter. The maximum UV nucleus concentration was 123,000 per c.c., and the steady state nucleus concentration was about 20,000 per c.c., or 16% of the maximum concentration. This may be compared to the percentage of about 28%, for the results of an experiment with cotton wool filtered air, plotted in Fig. 6.

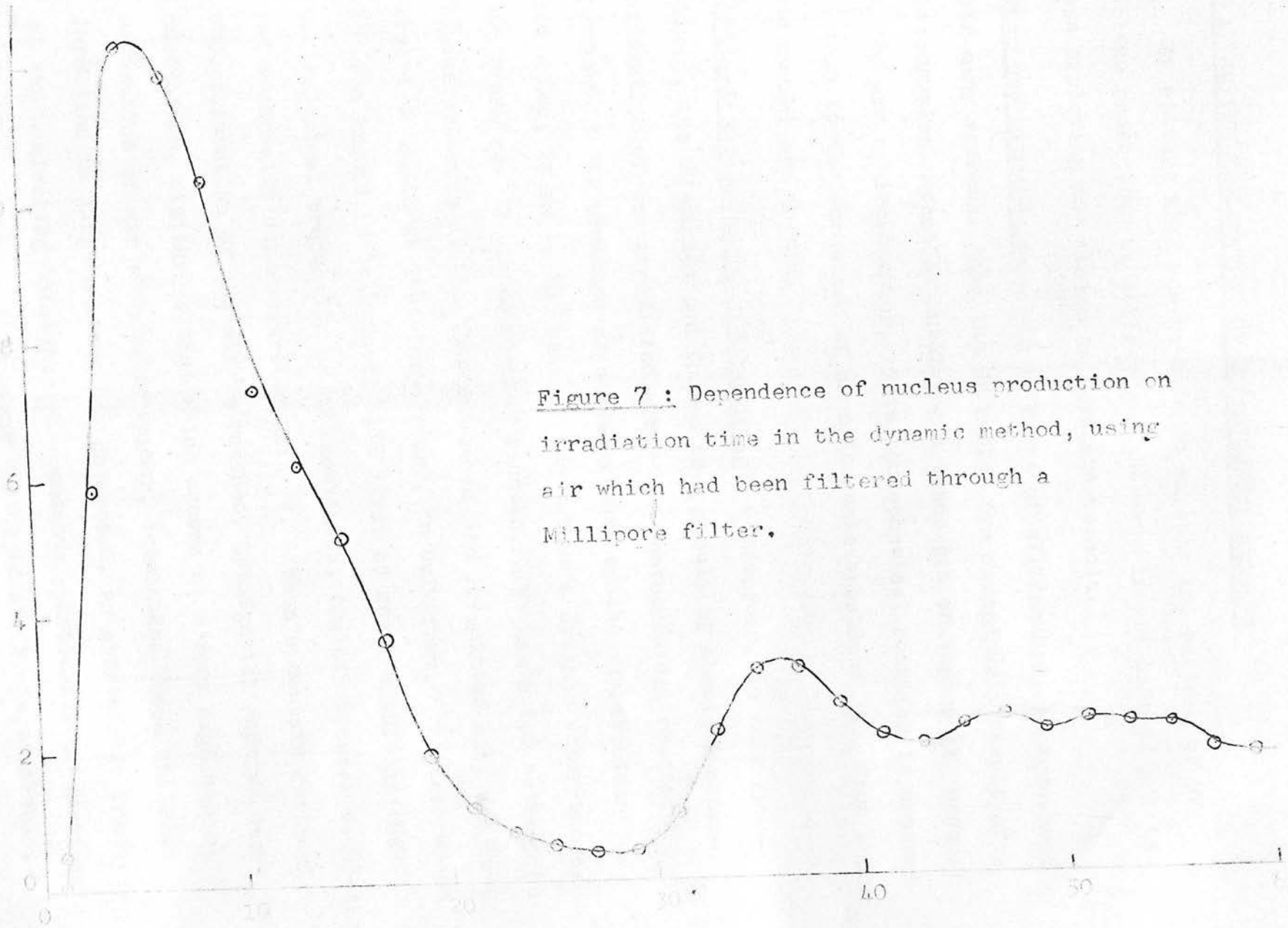


Figure 7 : Dependence of nucleus production on irradiation time in the dynamic method, using air which had been filtered through a Millipore filter.

AN ATTEMPTED EXPLANATION OF EXPERIMENTAL RESULTS

An attempt will now be made to explain the pattern of UV nucleus production as observed in the experiments carried out to date employing the static and dynamic methods.

Trace gas hypothesis: It is first of all assumed, in agreement with many workers, that the UV nuclei are formed as a result of a photochemical reaction involving a trace gas or vapour X present in the air on irradiation. This photochemical reaction is assumed to lead to the formation of a nucleogenic substance Y, from which the nuclei are formed.

Chemical supersaturation hypothesis: According to this hypothesis, the UV nuclei are formed as a result of chemical supersaturation of the irradiated air. The photochemical reaction product Y is produced at a steady rate by the ultraviolet radiation, if as is the case in the author's dynamic experiments, the trace gas X is constantly renewed. Y has a low saturation vapour pressure at the temperature of the irradiated air, and is a liquid or solid at that temperature, in bulk form. The case where Y is a liquid in bulk form, will first be dealt with. As the photochemical production of Y continues, the air becomes saturated, and eventually supersaturated with Y. When a certain critical supersaturation of the air is reached, substantial homogeneous nucleation, similar to that which occurs at a very high supersaturation of air with water vapour, commences. Once nucleus formation in large numbers has commenced, an appreciable fraction of the nucleating substance Y condenses physically or chemically on existing nuclei. This means that less of Y is available,

for the formation of new nuclei since the average supersaturation, which has passed through a maximum value, is now reduced. This is so, in spite of the fact that Y is still produced photochemically at the same rate as ever. The average supersaturation of the air with Y continues to decrease now, until eventually a steady state situation is reached, where a fixed fraction of Y is condensing on existing nuclei while the remaining fraction of Y leads to the formation of new nuclei. The supersaturation of the gas with Y varies from point to point in the gas. It is sufficiently high in the "spaces" between existing nuclei, to cause substantial homogeneous nucleation. It is low near existing nuclei, since Y is condensing on these nuclei.

The concentration of nuclei is expected to follow a fairly similar curve to the average supersaturation, with time. However initially there is no nucleus production, when the supersaturation of the air with Y is building up to the critical value for homogeneous nucleation, since the supersaturation is uniform throughout the gas. A peak occurs in the nucleus concentration, corresponding to the peak in supersaturation, (or concentration of Y in the gas). Similar to the supersaturation, nucleus production falls after its maximum value, until it reaches its steady-state value. Thus this hypothesis explains qualitatively the "time delay", the peak nucleus concentration, and the steady state nucleus concentration, observed in the dynamic experiment.

According to the chemical supersaturation hypothesis, the nuclei present in the air during the constant steady-state rate of production, in the dynamic experiment, ought to be larger in size than the nuclei present in the air at the time of peak nucleus concentration.

According to this hypothesis, the pattern of nucleus production in the static method ought to be similar to that in the dynamic method, except that nucleus production would not reach a steady state value, but would fall eventually to zero as trace gas X is consumed in the photochemical reaction leading to production of Y. In the author's experiments with the static method, a continuous fall in nucleus concentration, after peak nucleus concentration, has indeed been observed.

If the nucleogenic substance Y is a solid, in bulk form, at the temperature of the irradiated air, the nuclei produced are probably in the form of crystals, rather than droplets, as was assumed above. A rather different treatment is necessary in this case, but the general pattern of nucleus production should be quite similar in both cases.

Evaluation of the critical supersaturation for substantial nucleation in the dynamic experiment:

It is a difficult problem to evaluate theoretically the critical supersaturation S^X at which substantial homogeneous nucleation sets in, under the conditions of the dynamic experiment. Volmer and Flood (1934)[43] derived and verified a relationship

$$\log S^X \propto \left(\frac{\gamma}{T}\right)^{3/2} \frac{M}{\rho} \qquad (1)$$

where S^X is the critical supersaturation for a particular nucleation rate, achieved after an adiabatic expansion in a cloud chamber, for a liquid, with surface tension γ, molecular weight M, and density ρ. T is the absolute temperature of the gas.

If S^X is known for a particular liquid, then S^X for other liquids whose constants are known, may be calculated from equation (1). Mason[44] quotes a value of 3.74 for S^X for water, measured experimentally for a final temperature of 19.1°C, after adiabatic expansion in a cloud chamber, by Powell (1928).

As an example of a photochemical reaction leading to nucleus formation, we will take the photo-oxidation of sulphur dioxide which leads to the formation of nuclei consisting partly or wholly of sulphuric acid (see Dunham[30], Leighton[45]). It is thought by many workers, such as Aitken[11], Hoppe[31], that photochemical reactions involving sulphurdioxide lead to condensation nucleus formation in polluted air.

Using the value of $S^X = 3.74$ for water, S^X for sulphuric acid (γ = 55.0 dyne/cm., M = 98, ρ = 1.84 gm/c.c) is calculated to be 10.6, for an adiabatic expansion at a final temperature of 19.1°C. As was mentioned before, however, substantial nucleation would not occur at this supersaturation, under the conditions of the dynamic experiment, where sulphuric acid molecules would be produced at a steady rate. However this sort of treatment of the problem may give an indication of the relative critical supersaturations for substantial nucleation, under the conditions of the dynamic experiment, for various liquids.

Dunham's treatment of the problem:

Dunham[46] used a computer to solve equations derived from a consideration of the Becker-Doring theory of homogeneous

nucleation, and the Mason theory of droplet growth, for a system where a nucleating substance is being produced at a constant rate, as in a photochemical reaction, using an experimental set-up similar to that used in the author's dynamic experiments. For formation rates of 10^7 molecules/c.c. and 10^9 molecules/c.c. for sulphuric acid, this theory predicted that the maximum supersaturations reached at $15^{\circ}C$, would be 43,0 and 65.3 respectively, both extremely high. He produced a curve of nucleus concentration against time for a hypothetical case involving formation of water molecules at a steady rate. This curve shows a "time delay" before nucleus production begins, but there is no peak nucleus concentration. The nucleus concentration increases rapidly with time, after the initial time delay, to a steady high concentration, and remains at that high concentration. This seems strange since his curve for the concentration of molecules of water in the gas, (or supersaturation) against time shows a peak concentration, shortly after the commencement of substantial nucleation. His curve then shows a gradual fall of the concentration of molecules of water in the gas, to a "steady-state" value, the gas still remaining supersaturated.

Dunham's curves for nucleus concentration and concentration of molecules of the nucleating substance against time, agree with the author's chemical supersaturation hypothesis, except for the one important exception, that the nucleus concentration does not show a peak value or a consequent fall to a much lower steady-state value.

It must be stated that the chemical supersaturation hypothesis

as put forward here by the author, has been rather oversimplified. For example the photochemical reaction involving X and leading to formation of Y may take place by a number of steps, and there may be some intermediate reactions and reaction products, which must be taken into account in a rigorous treatment of the problem. Also, the nuclei may be formed from other substances as well as Y. For example, in the case of the photo-oxidation of sulphur dioxide, in air, it seems likely that the nuclei formed will contain both sulphuric acid and water. In this case a quantitative application of the chemical supersaturation theory would be extremely complicated, since the vapour pressures of at least two components, sulphuric acid and water, are involved.

Alternative hypotheses:

Some alternative hypotheses, to explain features of the pattern of nucleus production in the static and dynamic experiments, will now be briefly discussed.

Time delay due to diffusion losses:

A possible explanation of the "time delay" is as follows: The nuclei produced in the first minute of UV irradiation, are very small. Small nuclei diffuse more rapidly than large ones. Thus the small nuclei produced in the first minute of irradiation disappear very quickly from the gas, by diffusing to the walls, of the flask, connecting tubing, and counter, and are thus not detected. Any nuclei surviving in the counter, may be too small to be detected, at the standard volume expansion ratio of 1.147 used, for the expansion in the counter. On further irradiation,

coagulation causes the appearance of larger nuclei, which remain longer in the gas, because they diffuse more slowly than the smaller nuclei. These larger nuclei are therefore detected in the nucleus counter, at the standard expansion ratio.

C.T.R. Wilson[16] noticed that the nuclei produced by a weak UV radiation in air, in a glass/quartz tube, disappeared very quickly from the gas when the irradiation was stopped, and needed large expansions to condense on them. The nuclei produced by a stronger radiation did not disappear so quickly at all, and were quite easily detected. The nuclei seemed to grow bigger with continued irradiation. Wilson suggested that the nuclei diffused much more slowly to the walls of the container, when they were big, and that thus many more of them were detected.

Possible emission of nuclei from the flask walls:

There is a possibility that the occurrence of a peak nucleus concentration is due to the emission of nuclei or nucleogenic material from the walls of the flask, on irradiation. A transient production of nuclei would therefore occur, at the commencement of irradiation, in a manner similar to the transient production of nuclei by heated surfaces of metal, glass, etc., due to occluded impurities on the surfaces of these substances. This type of transient nucleus production by heated surfaces has been discussed by O'Connor, Sharkey and O'Brolchain[47] and by the author[26]. The transient production of nuclei, by the flask walls, on irradiation may be superimposed on a steady nucleus production in the gas, giving a curve similar to that found in the dynamic experiment.

The dubious observation that maximum nucleus concentration increases with increased flushing time, supports this hypothesis. The flask walls would absorb more of the impurity responsible for this transient nucleus production, from the larger volume of gas passing over the flask walls, for the longer flushing times. However the flask walls would become saturated with the impurity eventually, and no further amount would be absorbed.

Secondary peaks of nucleus concentration have been observed several times, in dynamic experiments. Fig. 7 shows a small secondary peak. Quite large secondary peaks have been observed at various times after the occurrence of the primary or initial peak. These observations do not agree with the above hypothesis, since according to this hypothesis, only one peak should occur, and this would be at the commencement of irradiation.

Peak nucleus concentration due to coagulation:

This hypothesis suggests that the observed sharp fall in nucleus concentration, after the occurrence of the maximum concentration, in both the static and dynamic experiments, is due to the fact that when new nuclei are formed, they are very small, and thus combine very rapidly with existing nuclei, since they diffuse very rapidly through the gas. Thus when new nuclei have been produced, only a fraction of them remain uncombined with previously formed nuclei, at the time of measurement of nucleus concentration. As a result, less new nuclei are detected, when there is a large concentration of nuclei already present. The increase in the total nucleus concentration, before the occurrence of peak concentration,

is due to the fact that the rate of production of new nuclei, which remain uncombined with previously formed nuclei, is greater than the rate of loss of all nuclei through mutual coagulation and diffusion to the walls of the flask, and other possible causes. After the occurrence of peak nucleus concentration, the rate of loss of all nuclei exceeds the rate of formation of new nuclei, which remain uncombined with previously existing nuclei.

The author does not find this hypothesis convincing, since there is no reason given why the rate of loss of all nuclei should overtake the rate of formation of uncombined new nuclei, at the time of the occurrence of peak nucleus concentration.

Possibility of nuclei absorbing initial trace gas X:

It is possible that the decrease in nucleus concentration after peak concentration, in the dynamic experiment, is due to the nuclei existing in the gas now absorbing the trace gas X, and hence reducing the amount of X available for the photochemical formation of the nucleogenic substance Y .

Peak concentration not due to variation in radiation from the UV lamp:

It was thought that the pattern of nucleus production observed in the dynamic and static experiments, might be due to a variation in the radiation of the UV lamp, during the first hour that it was switched on. For this reason, the UV lamp was switched on two hours before commencing irradiation of the gas in one dynamic experiment. The pattern of nucleus production was the same as it always was in this experiment. Therefore the pattern of nucleus production in

the dynamic and static experiments is not due to any variation in the radiation of the UV lamp with time.

In another experiment, the total intensity of the UV lamp, was observed to remain constant, over a period of one hour, after the two minute "run-up" time. This was done by monitoring the light at a given distance from the lamp, by means of a photocell connected to a microammeter.

The various hypotheses described above, will be discussed further in the light of results from other experiments described in later parts of this work.

Results of other workers:

Goetz and Kallai (1963)[48] observed that existing latex nuclei grew to a larger size when exposed to UV radiation, than when they were not irradiated, probably due to the condensing on them of some photochemical reaction product. They found that whenever an "insufficient" number of nuclei existed in the irradiated air, some new particles, very small, and of a different constitution to the later nuclei, were produced. There were absent whenever enough total nuclear surface was present. Goetz and Pueschel (1965[49] found that a higher concentration of nuclei were produced, by irradiation of a mixture of nitrogen dioxide and octene-I in air, when no nuclei already existed in the gas, on irradiation, than if such nuclei existed. When nuclei already existed in the gas on irradiation, the nucleogenic substance produced photochemically, condensed on the existing nuclei, to a large extent, and formed relatively few new nuclei.

These results certainly suggest that the fall in nucleus concentration, after peak concentration, in the dynamic and static experiments, is due to the condensing on existing nuclei of nucleogenic substance Y, which is being photochemically produced. They are therefore in general agreement with the author's explanation of peak nucleus concentration, under the chemical supersaturation hypothesis.

Doyle and collaborators[34,35], found patterns of nucleus production, similar to the author's, when they irradiated a mixture of sulphur dioxide and air, and also a mixture of sulphur dioxide, nitric oxide, and tetramethylethylene. These workers used an experimental procedure similar to the author's dynamic experiment. Their plots of nucleus concentration against time of irradiation show an initial peak concentration, with a consequent fall of nucleus concentration to a constant steady-state value. Their plots do not, however, show a well marked "time delay". It was estimated that only about 0.6 pphm of the sulphur dioxide was consumed, out of a total concentration of 24 pphm, at the time of the occurrence of peak nucleus concentration, during irradiation of the mixture of sulphur dioxide and air. This certainly shows that peak nucleus concentration is not due to early depletion of the sulphur dioxide.

Doyle and collaborators, also showed that the light scattering from the aerosol formed in these experiments, continued to increase with irradiation time, over the first hour of irradiation time, at least, although peak nucleus concentration occurred after a few minutes of irradiation time. This suggests that there were

more large nuclei present in the irradiated gas during the steady-state constant rate of nucleus production, than at the time of occurrence of peak nucleus concentration, since large nuclei are much more effective for light scattering, than small nuclei.

This result is in agreement, therefore, with the author's suggestion, under the chemical supersaturation hypothesis, that the nuclei present in the air during the constant, steady state rate of nucleus formation, in the dynamic experiment, ought to be larger than the nuclei present in the air at the time of occurrence of peak nucleus concentration.

EXPERIMENTS INVESTIGATING THE TRACE GAS HYPOTHESIS

A number of experiments were carried out in order to find out whether the presence of some trace gas or vapour X in the air was responsible for nucleus formation, on UV irradiation. In the first two experiments described, filtered air was stored in either a dry flask or in a flask containing water, for various periods of time, before irradiation, in order to find out if any drop occurred in UV nucleus formation, which would be consistent with the gradual removal of the trace gas X, by absorption on the inside of the flask or by being dissolved in water in the flask, or by being removed by some slow chemical reaction with some other substance present in the flask.

Effect of storing filtered air in the flask, on UV nucleus formation in that air.

Outdoor air which had been filtered through a cotton wool filter was enclosed in the flask overnight before irradiating it. The concentration of nuclei measured after irradiation for a fixed time, using the static method, was not appreciably different from the nucleus concentration produced in air which had been freshly filtered through cotton wool. When freshly filtered air was stored in the flask for periods of a ½ week and three weeks, the concentrations of nuclei produced in static irradiations for a fixed time were only 56°/o and 0.5°/o respectively, of the UV nucleus concentrations produced in a similar static irradiation of air which was freshly filtered through cotton wool.

Discussion of results

The results of this experiment suggest that possibly:

(1) A trace gas or vapour X responsible for UV nucleus formation was slowly absorbed on the inside of the flask during storage, and thus gradually removed from the air,

or

(2) A trace gas or vapour X responsible for UV nucleus formation was removed from the air in the flask by a very slow chemical reaction, with one of the main gases present in the flask, or with another trace gas or vapour present in the flask.

Effect of storing filtered air in a flask containing 400 c.c. of deionized water, on UV nucleus formation in that air.

It was decided now to store the air, before irradiation in a flask containing excess water, to find out if the trace gas X would be removed from the air more quickly than in a dry flask, by being dissolved in the water.

About 400 c.c. of deionized water was placed in the bottom of the flask, while it was being filled with outdoor air filtered through cotton wool, prior to a static irradiation. This water was left in the bottom of the flask during a 6.0 minutes static irradiation of the air in the flask. The concentration of nuclei produced in this 6.0 minute static irradiation was only 78,000/c.c., compared to a concentration of 280,000/c.c. produced in a dry flask shortly before. Freshly filtered air was not stored in the flask, containing the 400 c.c. deionized water, for periods of time of 30 minutes and 18 hours, before irradiating it. The concentrations of nuclei produced in 6.0 minutes static irradiations were only 9,900/c.c. and zero/c.c. respectively.

Discussion of results

Filtered outdoor air stored in a flask containing 400 c.c. of water loses its UV nucleus forming power much more quickly than the same air stored in a dry flask. This result is consistent with the idea that a trace gas or vapour X which is soluble in water, is responsible for UV nucleus formation. When there is 400 c.c. of water present in the flask, X begins to dissolve in the water until equilibrium is reached between the concentration of X in the gas and the concentration of X in solution in the water, according to Henry's law, (if the gas obeys Henry's law). For example, with 400 c.c. of water in the flask, it was calculated that three quarters of the sulphur dioxide in the flask would be in solution in the water, and only one quarter would be in the gas, at equilibrium, at room temperature, according to Henry's law. However, since sulphur dioxide in water is slightly ionized, there would in fact be more than three quarters of the total sulphur dioxide, in the water, at equilibrium, leaving less than one quarter in the air. Therefore the result of placing 400 c.c. of water in the bottom of the flask is to reduce the concentration of sulphur dioxide in the air in the flask to about one quarter of the original concentration. Water in the flask has a similar effect, in varying degree, on the concentration of other water soluble trace gases in the air in the flask. Thus the rate of UV nucleus production from trace gas or vapour X falls appreciably on storage in the flask containing excess water, if X is water soluble. UV nucleus production may fall to zero if the concentration of X in the air falls below a critical or threshold

concentration necessary for UV nucleus formation. Evidence for the existence of such a critical concentration is presented in a later part of this work. The water in the flask may remove completely trace gases, which are highly ionized in solution in water.

The partial reduction in UV nucleus production, in the author's experiment was probably due to a partial removal of X, equilibrium between the concentration of X in the gas and in the vapour not having been reached. The suppression of UV nucleus formation is probably due to a total removal of X from the gas, or to a reduction of the concentration of X in the gas below a critical concentration, necessary for UV nucleus formation.

UV nucleus formation in air which had been passed through a humidifier prior to irradiation.

It was now decided to pass the filtered air through a humidifier, prior to irradiation, as it was thought that the pattern of nucleus production might be informative, since some of the trace gas or vapour X assumed to be responsible for UV nucleus formation, should be removed by being dissolved in the water in the humidifier, if it is water-soluble.

Outdoor air which had been filtered through cotton wool was bubbled through deionized water in two gas washing bottles, connected in parallel, to reduce the resistance to the air flow. The air then passed through a millipore filter and then into the flask, where it was irradiated for various periods of time, ranging from 0.5 to 30.0 minutes, using the static method. The air, at a flow rate of 3.0 litres per minute, was passed through the Millipore filter after

bubbling through the de-ionized water, in order to remove any nuclei or spray formed by the bubbling of the air through the water. One half of the airflow or 1.5 litres per minute passed through each gas washing bottle, and each gas washing bottle contained 500 c.c. of de-ionized water. Test measurements of nucleus concentrations in the air were always made before irradiation, in order to make sure that the air was free of nuclei before irradiation. The static irradiations were not carried out in order of increasing irradiation times, but were carried out at randomly chosen irradiation times, between 0.5 and 30.0 minutes, over a period of three days. It was also found that the first irradiation made, on starting a "run" or series of experiments produced a nucleus concentration that was invariably higher than the average concentration produced in irradiations other than the first, for the same irradiation time. Therefore all such first measurements were rejected.

Fig. 8 shows the results of this experiment, as a plot of UV nucleus concentration against irradiation time. The pattern of nucleus production was rather similar to that found, using the static method, for outdoor air which had been filtered through cotton wool, but not humidified. The main differences between the two patterns of production may be noticed in Fig. 8, where the plot for air which has not been humidified is reproduced again, for ease of comparison.

(1) With the humidified air, the increase of nucleus concentration with irradiation time, was less marked, and the maximum nucleus concentration occurred at 13.0 minutes irradiation time, compared to 6.0 minutes for the air which had not been humidified.

(2) The peak in the nucleus concentration was flatter, for the humified air.

(3) The maximum concentration for the humidified air was only

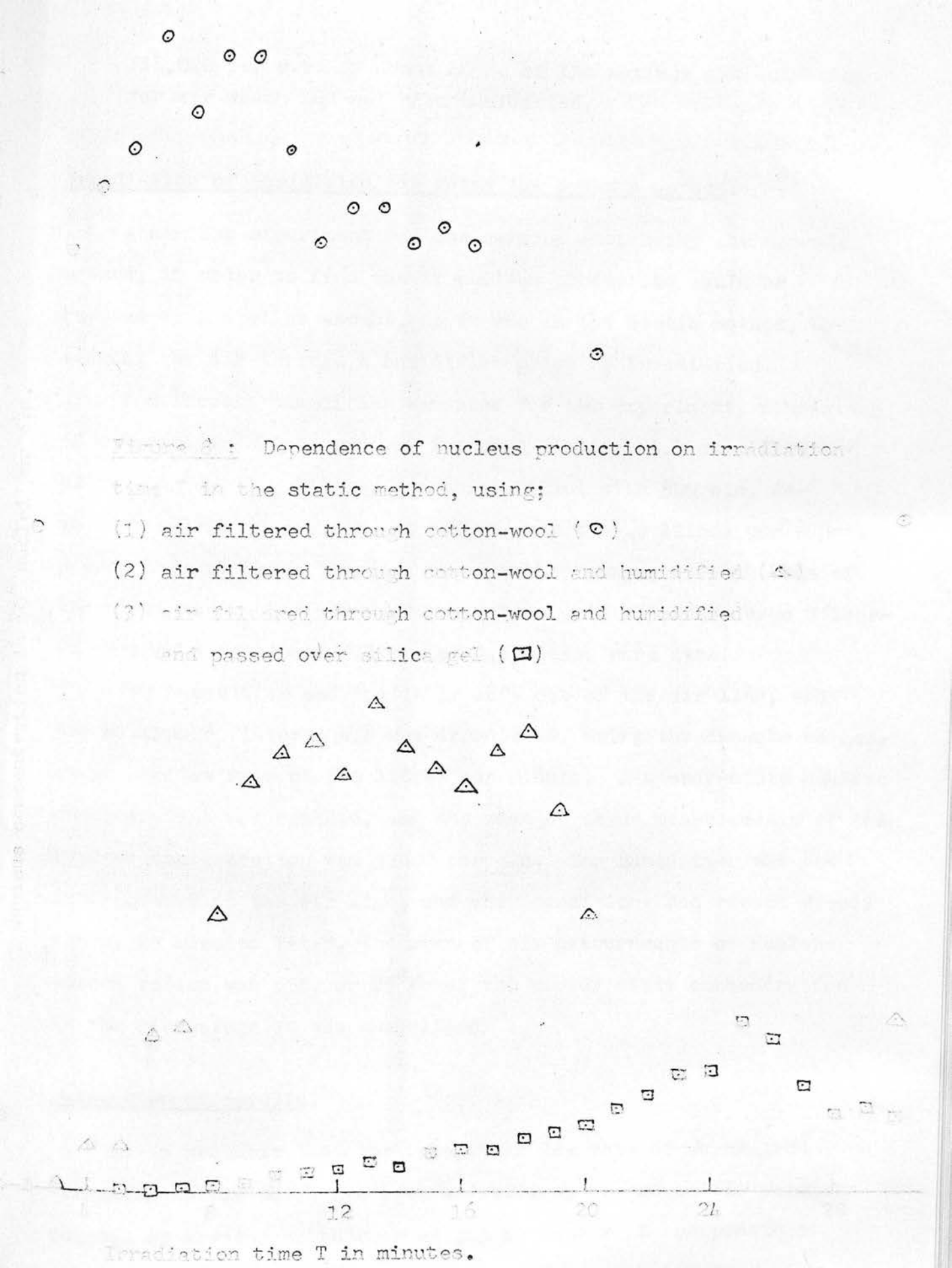


Figure 4 : Dependence of nucleus production on irradiation time in the static method, using;

(1) air filtered through cotton-wool (⊙)

(2) air filtered through cotton-wool and humidified (△)

(3) air filtered through cotton-wool and humidified and passed over silica gel (⊡)

Irradiation time T in minutes.

118,000 per c.c. or about 40°/o of the maximum concentration for air which had not been humidified.

Irradiation of humidified air using the dynamic method.

A similar experiment was now carried out, using the dynamic method, in order to find out if nucleus production would be reduced by a similar amount, as it was in the static method, by passing the air through a humidifier prior to irradiation.

A different humidifier was used for this experiment, consisting of a horizontal glass tube of internal diameter 5.4 cm., length 67 cm., volume 1.5 litres, one third filled with 500 c.c. de-ionized water. The water, at a flow rate of 3.0 litres per minute passed through brass tubes in clean rubber bungs, at both ends of the glass tube. The air used was outdoor air which had been filtered through a Millipore filter, of 1.2 micron pore size.

The humidifier was initially left out of the air line, and the Millipore filtered air was irradiated, using the dynamic method, at an airflow rate of 3.0 litres per minute. A steady-state nucleus concentration was reached, and the mean of three measurements of the nucleus concentration was 3,400 per c.c. The humidifier was now incorporated in the air line, and when conditions had become steady again, 45 minutes later, the mean of six measurements of nucleus concentration was 850, or 25°/o of the steady state concentration in the air before it was humidified.

Discussion of results.

It is probable that the relatively low rate of UV nucleus formation in air which has been humidified, is due to the partial removal of a water soluble trace gas or vapour X responsible

for UV nucleus formation. Some of the trace gas or vapour X would go into solution in the water, while the air was passing over the water, or bubbling through the water. The later occurrence of peak nucleus concentration, in the static experiment, is probably due in some way to the lowering of the concentration of X in the air, together with the saturation of the air with water vapour.

Agreement of results with those of other workers.

McGreevy and O'Connor[25] also found that humidified air, irradiated by sunlight formed a lower concentration of nuclei than air which had not been humidified. On the other hand, Mulcahy and Kuffel[29], found that production of UV nuclei in air and argon was similar, and showed the same increase with the water vapour pressure in the irradiated air. However these workers used ultra-violet radiation, reaching down to 2000A wavelength, and their UV nuclei were probably produced as a result of a completely different reaction from that occurring in the author's experiments.

UV nucleus formation in air which had been passed through a drying-tower containing silica gel, prior to irradiation.

It was decided to dry the filtered air, by passing it through a silica gel drying tower, prior to irradiation, in order to find out if the presence of water vapour in the air, at the time of irradiation, was essential for UV nucleus formation.

Static method: Outdoor air which had been filtered through cotton wool was now drawn into the flask, at the normal rate of 3.0 litres per minute, through a drying tower containing fresh,

unused, coarse silica gel. Silica gel is a commonly used drying agent. The flask was well flushed with this dried air, and then the air in the flask was irradiated, using the static method. There was absolutely no nucleus production, for irradiation times up to one hour.

Dynamic method: A silica gel tower and a bypass tube were placed in the airline between the cotton wool filter and the flask. By means of a three-way tap, it was possible to draw the air through either the silica gel tower or its bypass. The air was now irradiated with ultraviolet radiation, using the dynamic method, with the air passing through the silica gel tower bypass at the normal flow rate of 3.0 litres per minute. The experiment was carried out in this way, until steady state nucleus production was reached. The steady state nucleus concentration was about 150,000 per c.c., as is shown in the plot of nucleus concentration against time, in Fig. 9. At the time of 6.0 minutes in Fig. 9, the incoming air flow was diverted from the silica gel tower bypass tube, to the silica gel tower. As can be seen from Fig. 9, the UV nucleus concentration dropped to zero, over the next 12.0 minutes. It must be remembered that, due to the diffusion of existing nuclei and mixing of the air in the flask, it would be impossible to record a faster reduction in nucleus concentration.

At the time of 30.0 minutes in Fig. 9, the air flow was diverted back again to the silica gel tower bypass tube. It can be seen that after a small time lag, UV nucleus concentration increased rapidly to a maximum of 191,000 per c.c. and then fell gradually to its value at the beginning of the plot shown in Fig. 9.

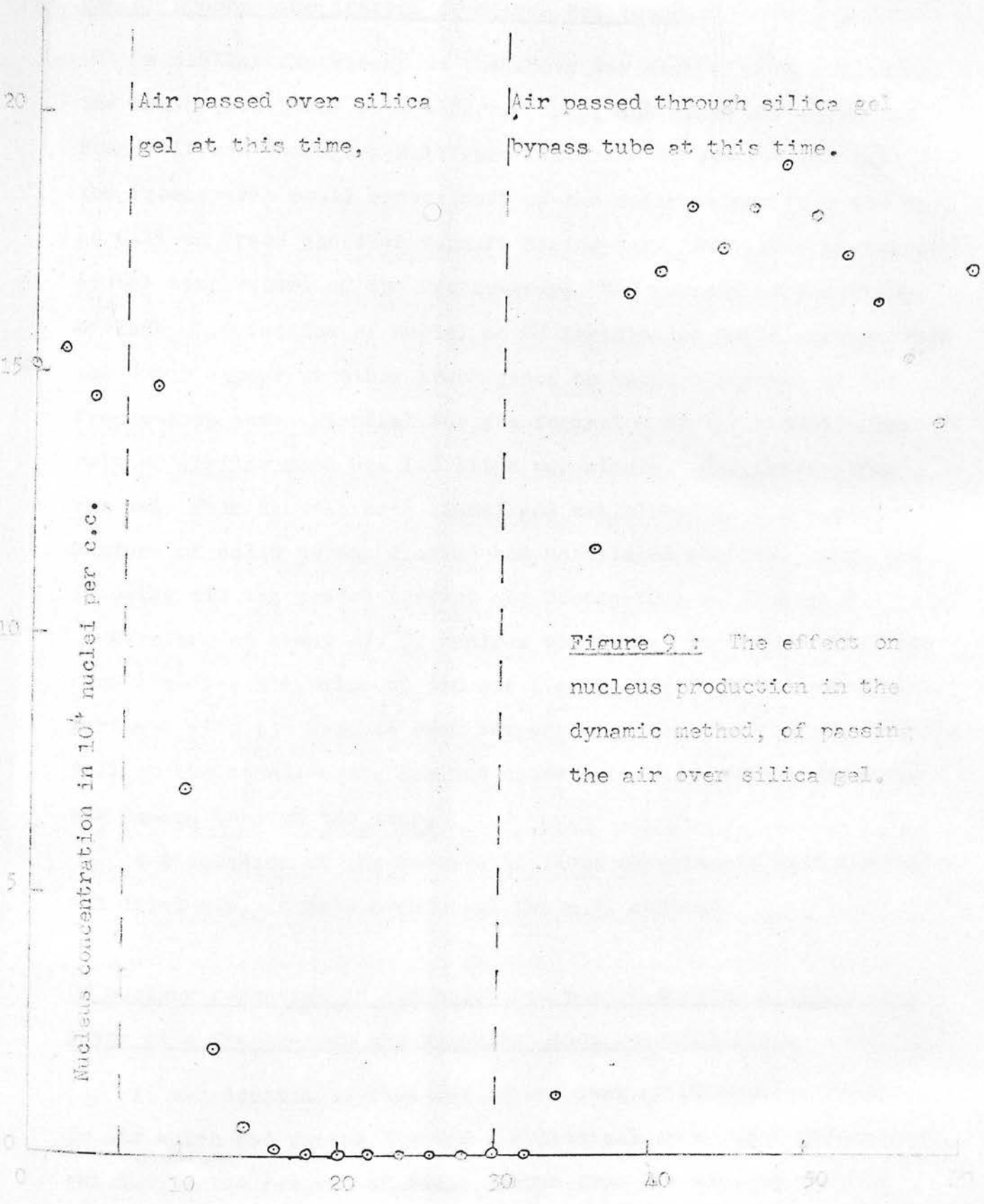


Figure 9 : The effect on nucleus production in the dynamic method, of passing the air over silica gel.

Use of Freeze-trap instead of Silica Gel tower.

A similar experiment to the above was carried out, replacing the silica gel tower with a freeze-trap, and using air which had been filtered through a Millipore filter. It was thought that the freeze-trap would remove most of the water vapour from the air, as well as trace gases or vapours having very low vapour pressures at the temperature of the freeze-trap. The consequent formation, or lack of formation of nuclei on UV irradiation would show whether the water vapour or other trace gases or vapours removed by the freeze-trap were essential for the formation of the nuclei. The rate of airflow used was 1.0 litre per minute. The freeze-trap was made from borosilicate glass, and was placed in a freezing mixture of solid carbon dioxide and methylated spirits. When the incoming air was passed through the freeze-trap at this cold temperature of about $-77^{\circ}C$, nucleus concentration dropped from its mean steady-state value of 560 per c.c. to zero. In a control experiment with the trap at room temperature, there was no appreciable fall in the steady-state nucleus concentration, when the incoming air passed through the trap,

A discussion of the results of these experiments with humidified and dried air, is held over until the next section.

UV nucleus formation in air which had passed through a silica gel tower or a freeze-trap and which was then re-humidified.

It was desired to find out if the lack of UV nucleus formation in air which had passed through a silica gel tower or a freeze-trap, was due to the removal of water vapour from the air, or whether some of the trace gas X assumed to be responsible for nucleus

formation, was also absorbed by the silica gel or removed by the freeze-trap. Therefore the air was re-humidified, after passing through these devices, and examined for UV nucleus formation.

The Static method:

Outdoor air which had been filtered through cotton wool, was drawn through a silica gel drying tower. It was then re-humidified by passing through two gas washing bottles, connected in parallel, each containing 500 c.c. of de-ionized water. The air was finally passed into the flask through a millipore filter, in order to remove any nuclei formed by bubbling in the gas washing bottles. The air flow rate was the normal 3.0 litres per minute. The air was now irradiated for various periods of time, using the static method. Nuclei were produced again, and the plot of UV nucleus concentration against irradiation time shown in Fig. 8, had a similar shape to the plots found with untreated filtered air, and with humidified filtered air, both of which are shown in Fig. 8 for comparison. However, the maximum concentration reached in the present case was only 41,600 per c.c. This is about 15°/o of the maximum concentration for air filtered through cotton wool, but otherwise untreated, and about 35°/o of the maximum concentration for air filtered through cotton wool and then humidified. The maximum concentration in the present case occurred at 25.0 minutes irradiation time, compared with occurrence at 6.0 minutes and 13.0 minutes for the untreated filtered air and the humidified, filtered air respectively. In the present experiment, the increase of UV nucleus concentration with irradiation time, was extremely slow. There was no appreciable nucleus concentration produced until the irradiation time was 5.0 minutes, at which time the nucleus concentration was 210 per c.c.

The Dynamic method:

In the dynamic experiment described on page 56 it was stated that the mean steady state concentration of UV nuclei was 560 per c.c. initially. When the incoming Millipore filtered air was now asssed through a freeze-trap at a temperature of $-77^{\circ}C$, the nucleus concentration dropped to zero. In a continuation of this experiment, the incoming Millipore filtered air was passed through the same freeze-trap, and then through the humidifying tube described in a previous section of this work. Nucleus production was partly restored, reaching in 50 minutes a fairly steady value of about 70 per c.c.

Sulphur Dioxide test:

As sulphur dioxide is one of the trace gases in the atmosphere suspected of leading to UV nucleus formation, it was attempted to find out if sulphur dioxide was removed from the filtered air, on passing through a silica gel tower or a freeze-trap and a humidifier.

Outdoor air which had passed at a flow rate of 1.6 litre per minute through (i) a silica gel tower, and (2) a freeze-trap, in a freezing mixture at $-77^{\circ}C$ and a humidifying tube, in series, was tested for sulphur dioxide concentration, using ammoniacal zinc nitroprusside test papers (see page 127). No sulphur dioxide was detected, although there was always an appreciable sulphur dioxide concentration in outdoor air. However these tests were not considered satisfactory, because in case (1), the test paper, which is moisturized by having some glycerol in the reagent mixture, may have been dried out and thus desensitized by the silica gel dried air passing through it; in case (2) the test paper was drenched by the water-saturated air passing through it, and this occurrence may also

have desensitized the test paper.

Megaw and Wiffen[50], found that a freeze-trap consisting of a number of small vessels in series, immersed in a freezing mixture of solid carbon dioxide and acetone, reduced the sulphur dioxide content of the air by only 10% to 15%.

Summary of Results of Recent Experiments

In these experiments filtered air was passed, before irradiation through

(1) a humidifier

(2) a drying tower containing silica gel

(3) a freeze-trap at a temperature of -77°C

(4) a silica gel tower and a humidifier

(5) a freeze-trap and a humidifier.

Results were as follows:

(a) Maximum UV nucleus concentrations in cases (1) and (4) using the static method of irradiation, were only 40% and 15% respectively of the maximum concentration for normal untreated filtered air.

(b) The maximum UV nucleus concentration in cases (1) and (4), using the static method of irradiation, occurred at irradiation times of 13.0 minutes and 25.0 minutes respectively, compared with 6.0 minutes for untreated filtered air.

(c) No UV nuclei were produced in cases (2) and (3).

(d) UV nucleus production was slightly restored, in cases (4) and (5).

(e) No sulphur dioxide was detected in the air in cases (2) and (5), although there was some always present in untreated air. However the sulphur dioxide test used was not considered satisfactory in these two cases.

Discussion of results.

The filtered air probably lost a very high percentage of its water vapour content, in passing through the silica gel tower, and through the freeze-trap, at a temperature of -77°C, The air, in passing through the silica gel, probably also lost a fraction of trace gases absorbed by the silica gel. The silica gel used, certainly absorbs some trace gases and vapours, including sulphur dioxide, but detailed information on this absorption was not available. The air in passing through the freeze-trap at a temperature of -77°C would, to various extents, lose trace gases and vapours whose saturation vapour pressures at -77°C are lower than their respective partial pressures in the filtered air, at room temperature. From the author's experimental results it seems that water vapour must be present at the time of irradiation of the air, otherwise UV nuclei will not be produced. No nuclei were produced in the irradiated dry air, which was then isolated in the counter, and saturated with water vapour, from the moist ceramic lining of the counter. UV nuclei were again produced in the air which had passed through a silica gel tower, when water, and only water was added, before UV irradiation.

It is not known why the occurrence of peak nucleus concentration is delayed when the air is humidified, or when the air is passed through silica gel and then re-humidified. This delay in the first case, may be due to the fact that the concentration of the trace gas or vapour X, assumed to be responsible for nucleus formation, is reduced, while the concentration of water vapour in air is increased. This would result in an increase of the ratio of the

concentration of water vapour in the air to the concentration of reaction product Y, which is assumed to be formed photochemically from X. If the UV nuclei consist of Y plus water, the ratio of water to Y in the nuclei would be higher in this case, than in the case of nuclei produced in untreated, filtered air. In other words, if the nuclei consist of a solution of Y in water, the solution in this case would be more dilute. This result might cause a slower rate of growth of the nuclei, especially if Y is hygroscopic. In air which had passed through silica gel, and was then re-humidified, the ratio of water to Y in the nuclei would be still higher, since both the silica gel and the water in the humidifier, would remove some of X.

The restored nucleus production in the air which had passed through silica gel or a freeze-trap, and was then re-humidified, may on the other hand be due to the desorption of the trace gas X, which was already absorbed on the inside of the glass in the flask. Thus, although the silica gel or the freeze-trap, may have removed all the X from the air passing through them, nevertheless the concentration of X in the air in the flask may have been partly restored, by this desorption of X, which was previously absorbed on the inside of the flask, when air containing X was passing through it. Dunham[30] obtained evidence that sulphur dioxide, at a relatively high concentration in air, was absorbed by a glass surface, and later liberated when air with a relatively low concentration of sulphur dioxide was in contact with this glass.

The partial restoration of UV nucleus formation, when air passed through silica gel or a freeze-trap, is re-humidified, may be due to

the fact that more than one trace gas or vapour takes part in UV nucleus formation. Thus, one or more of these trace gases or vapours would be removed completely by the silica gel and humidifier; or by the freeze-trap and humidifier. The remaining responsible trace gases or vapours, not very soluble in water, would not be completely removed. However, if more than one trace gas or vapour is responsible for nucleus formation, it seems that for all such trace gases or vapours, water vapour must be present in sufficient quantity in the air, on irradiation, otherwise they will not lead to nucleus formation.

Attempted consumption of trace gas or vapour X, assumed to be responsible for UV nucleus formation:

It was now reasoned that if a photochemical reaction involving a trace gas or vapour X, was responsible for UV nucleus formation, then an appreciable fraction of the amount of X present in the air before irradiation ought to be consumed on prolonged irradiation. Suppose that the nuclei formed as a result of this prolonged irradiation were somehow removed from the air. Then since the concentration of X in the air had been reduced, a further irradiation for a standard period of time ought to produce a lower concentration of nuclei than were produced in a first irradiation of the air, for the same period of time.

In the following experiment, it was decided to remove the nuclei from irradiated air, by leaving the air isolated in the flask, overnight after irradiation, so that nuclei produced in this first irradiation would be lost through mutual coagulation, diffusion to the walls of the flask, settling to the bottom of the flask, under gravity, and other possible causes.

Outdoor air, which had been filtered through cotton wool, was exposed to the ultraviolet radiation, using the static method, as normal. Two separate irradiations of 6.0 minutes resulted in a UV nucleus concentration of 285,000 per c.c. Another 6.0 minutes irradiation of freshly filtered air was carried out, but this time the irradiated air was left isolated in the flask, overnight for 18 hours. Another 6.0 minute UV irradiation after this storage period, resulted in a UV nucleus concentration of 274,000 per c.c.

It is confirmed in a later control experiment, that only a negligible fraction of the nucleus concentration produced even in a one hour irradiation, remain in the flask, after 18 hours storage. It seemed therefore that only a very small fraction of the trace gas or vapour within the limits of experimental error, had been consumed in the first 6.0 minutes irradiation.

The experiment was now repeated, but the first irradiation time was increased to one hour, after which the air in the flask was left overnight, for 18.5 hours. A static irradiation of 6.0 minutes immediately before this first irradiation, resulted in a UV nucleus concentration of 300,000 per c.c. A 6.0 minutes static irradiation of the isolated air in the flask, after the 18.5 hours storage time, resulted in a much reduced concentration of 41,500 nuclei per c.c. A control experiment showed that the concentration of nuclei left in the flask, after making a one hour irradiation of outdoor air filtered through cotton wool, and then leaving the irradiated air isolated in the flask for 18.5 hours, was only 530 per c.c., so that the vast majority of nuclei produced in the first irradiation had indeed been removed from the air. It was shown in a previous experiment that UV nucleus formation in air which had been left for 18 hours in a dry flask, was not appreciably different from the nucleus formation in freshly filtered air.

Discussion of results:

The results of this experiment are consistent with the hypothesis that a trace gas or vapour X is consumed in a photo-chemical reaction, leading to UV nucleus formation. The results

also suggest that very little of X is consumed by the first 6.0 minutes of irradiation, the time of occurrence of maximum nucleus concentration, and that the assumed photochemical reaction is a relatively slow one. It has been already mentioned that Doyle and co-workers[34,35] found that only 2.5% of sulphur dioxide was consumed at the time of occurrence of maximum nucleus concentration, during the photo-oxidation of sulphur dioxide. The speed of the photochemical reaction would, of course, depend on various factors such as the intensity of the ultraviolet light, the transmission of the material of the irradiation chamber, for ultraviolet light, etc. The results of the author's experiments suggest that a large percentage of the trace gas or vapour X was consumed, after irradiation for a period of one hour, as the UV nucleus concentration produced in a 6.0 minute irradiation of this air, after it had been left overnight, was only about 14% of the concentration produced in filtered air which had not been previously irradiated.

Re-circulation of irradiated air, using the dynamic method:

It was decided to filter air which had been irradiated, using the dynamic method, and to pass the same air, after filtration, into the flask for a further irradiation. This process of re-circulation would be repeated several times, with no fresh air being introduced into the circuit. Each filtration would remove the UV nuclei produced in the last irradiation. Therefore, if a trace gas or vapour X is responsible for UV nucleus formation, it would be gradually consumed, so that UV nucleus formation, in

the planned experiment, would fall, as the air was re-circulated.

A peristaltic pump was used in order to provide the airflow, since it was necessary to use a pump that did not contaminate (i.e. by oil) the air passing through it. A peristaltic pump grips a flexible tube, usually of silicone rubber, between a fixed curved plate, and a rotating divided drum. The rapid rotation of the divided drum pushes little parcels of the air along the flexible tubing. Airflow rates of up to 3 litres per minute can be provided in this way.

The dynamic experiment was first of all carried out as usual, except that:

(1) an airflow rate of 1.5 litre per minute was used.

(2) A silica gel drying tube was not placed in the air line before the rotameter.

(3) The peristaltic pump was used to draw the outdoor air through the cotton wool filter, into the flask.

When the steady state nucleus concentration was reached, at a mean value of 57,400 per c.c., the already irradiated air was now re-circulated through the flask, by connecting the outlet of the pump to the inlet of the cotton wool filter. Therefore the air would be irradiated again and again, being filtered in between every irradiation, to remove nuclei produced in the last irradiation. The arrangement of apparatus at this stage is illustrated schematically in Fig. 10. The nucleus concentration in the air after passing through the flask, was checked over the next 12 minutes, and found to drop to 45,000 per c.c. in this time. The air was now allowed to re-circulate, without making any more measurement of nucleus concentration, since this involved introducing

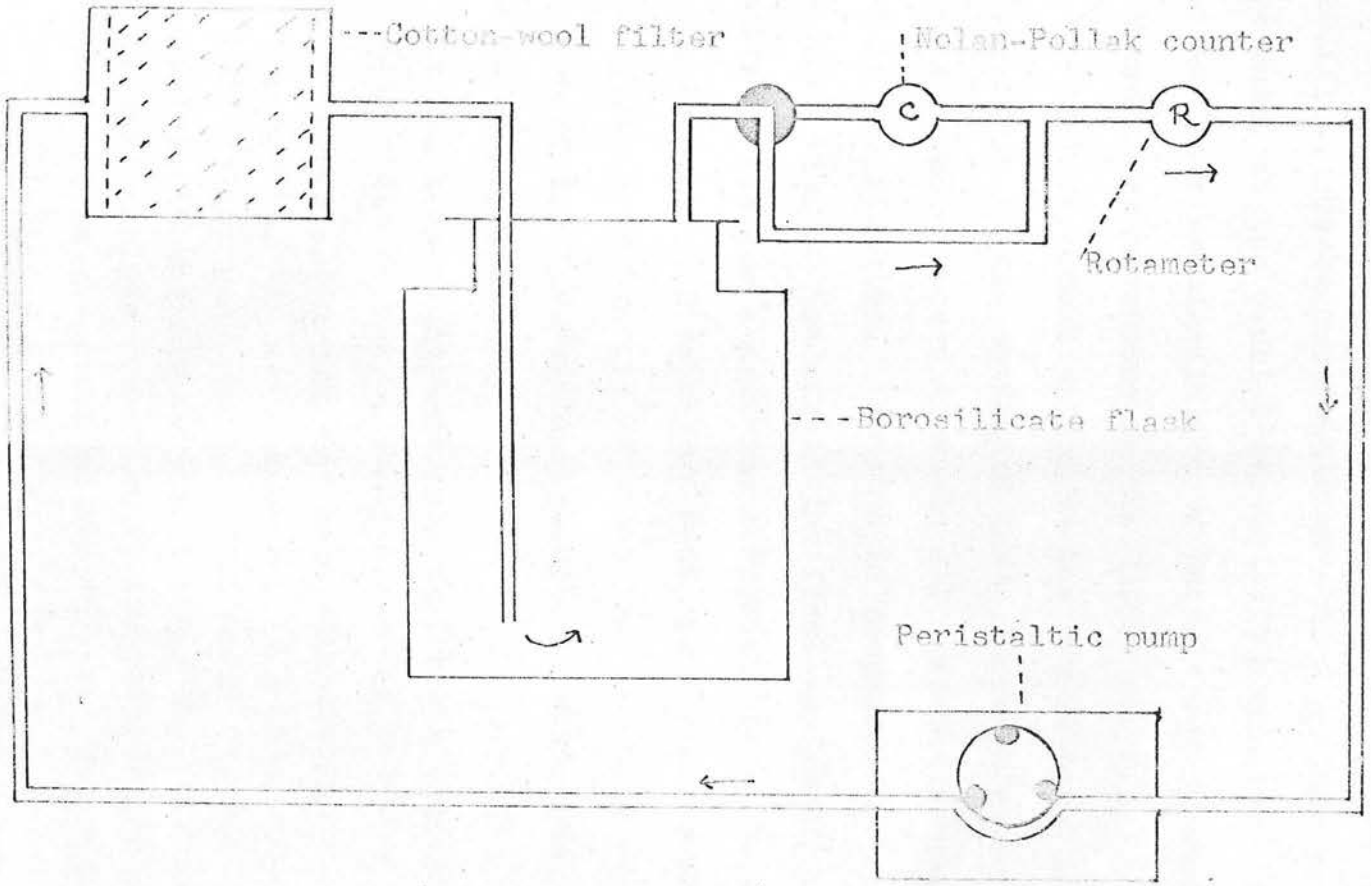


Figure 10 : The arrangement of apparatus for re-circulation of the irradiated air, using the dynamic method

a little filtered room air, used in providing the overpressure in the counter into the otherwise isolated, circulating air. Furthermore, the air passing through the counter, with its moist ceramic lining, would lose water soluble trace gases, and would be humidified. Three more measurements of nucleus concentration were made, at the usual interval of 2.0 minutes, starting 43 minutes after re-circulation of the air had commenced. The mean of these three measurements was 25,000 per c.c., or about 44% of the nucleus concentration at the beginning of re-circulation of the air. It was estimated that, on average, the air was re-circulated about seven times in all. As the average residence time in the flask was 4 minutes 20 seconds, the average total residence time of the air in the flask was about 30 minutes. The results of the above experiment suggest that a 30 minute exposure of the filtered air to the UV radiation, reduced the UV nucleus forming power of the air by about 56%, possibly due to the consumption of X. However this result has since been found to be open to doubt, because

(1) It has been found that passing the air through the cotton wool filter alters the UV nucleus forming power of the air.

(2) The peristaltic pump may have contaminated the air passing through it. It was discovered in a later experiment, that the peristaltic pump produces very large numbers of condensation nuclei, in the air passing through it. A short investigation of this nucleus formation by the peristaltic pump was carried out, and is described in Appendix I. The nuclei produced in the peristaltic pump, would have been removed by the cotton wool filter, in the present experiment, but nevertheless their presence may have contaminated the air.

A DOUBLE IRRADIATION OF FILTERED AIR, USING TWO FLASKS, TWO FILTERS AND TWO ULTRAVIOLET LAMPS.

Due to the uncertain results of the last experiment, in which the peristaltic pump was used, a new experiment was devised. Fig. 11 shows the experimental set-up. In this arrangement, outdoor air was drawn through a 1.2 micron pore size Millipore filter, one borosilicate glass flask, a second 1.2 micron pore size Millipore filter, and a second borosilicate glass flask, similar to the first. The air then passed as usual through either the Nolan-Pollak counter or the counter bypass tube. Each flask could be independently exposed to its own ultraviolet lamp, at the standard separation of 15.7 cm. from lamp to flask. The irradiation of the air in each flask was commenced, as usual, by removing the shutter between that flask and its UV lamp. Each flask, with its UV lamp, was mounted in a large case with a black interior, and both lamp and flask were cooled by a large fan, as usual. It may be noticed that the experimental set-up is exactly the same as for the simple dynamic method, except that the incoming air passed through two filters and two flasks, instead of one filter and one flask.

The reasoning behind the experiment was as follows. Let us assume that originally, only flask (2), (nearest to counter), was exposed to the UV radiation, using the dynamic method, and that steady state UV nucleus concentration had been reached. If flask (1) were now also exposed to UV radiation, there ought to be a reduction in the rate of nucleus formation in flask (2), since

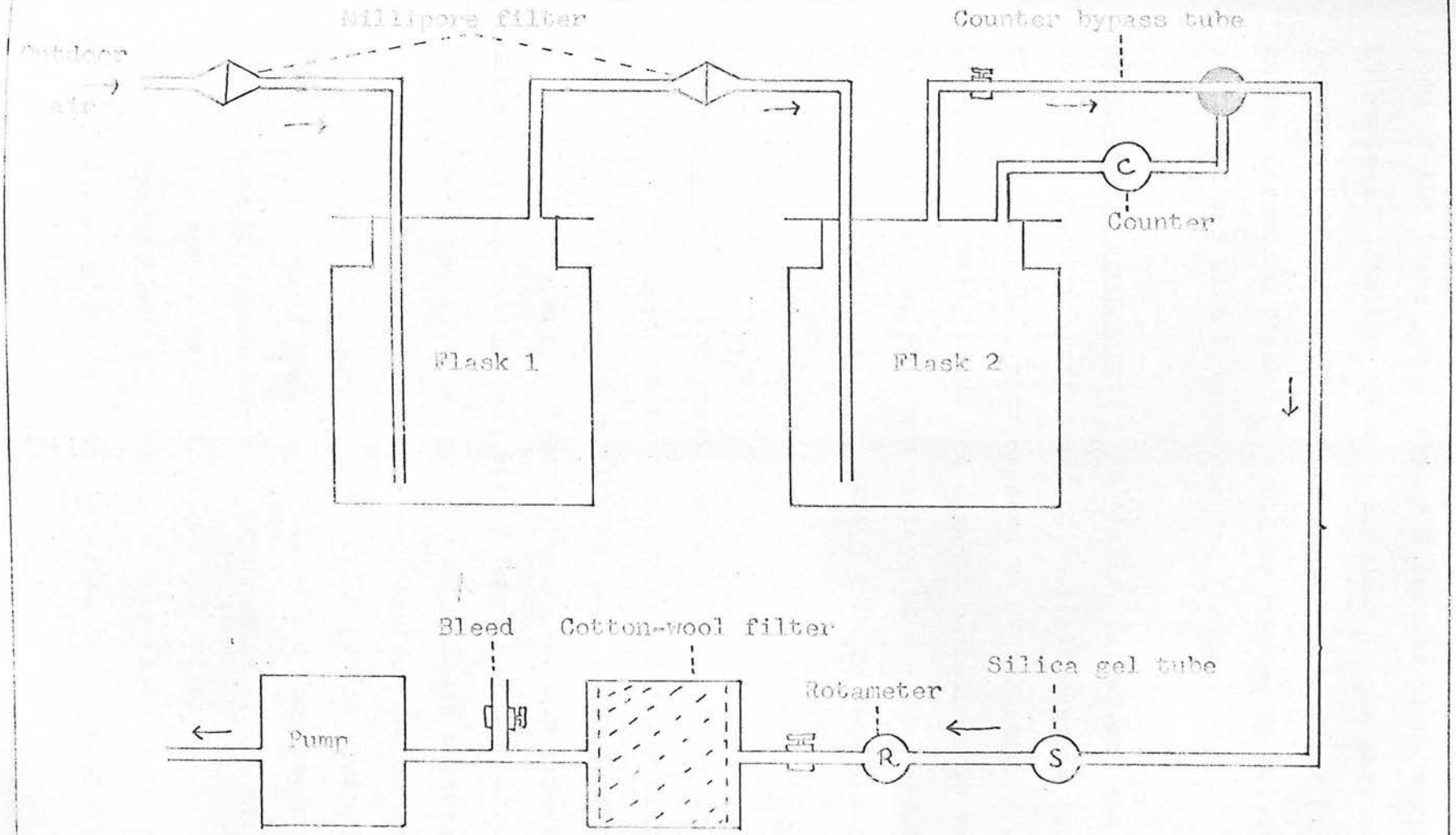


Figure 11 : The schematic arrangement of apparatus for the "double" irradiation of Filtered Air. The arrows show the direction of airflow.

some of the trace gas or vapour X assumed to be responsible for UV nucleus formation would be consumed by the photochemical reaction leading to UV nucleus formation in flask (1). The UV nuclei formed in flask (1) would be removed by filter (2) which is in the air line between the two flasks.

Experimental procedure: Initially, the extent and pattern of nucleus formation in filtered outdoor air passing through each flask, individually, when exposed to UV radiation from its own lamp, was checked, using the dynamic method. This was in order to ensure that the rate and pattern of nucleus formation in each flask was approximately the same. This in fact was observed to be the case.

Experiment I: The exact arrangement of apparatus illustrated in Fig. 11 was used. Both flasks were initially flushed with Millipore filtered outdoor air, as usual prior to commencing a dynamic experiment. Flask (2) only, was now exposed to the ultraviolet radiation from its UV lamp, and the nucleus concentration in flask (2) was measured at 2 minute intervals. The rate of air flow was 3.0 litres per minute. The nucleus concentration measured in the air from flask (2) is plotted against irradiation time in Fig. 12. Time $T = 0$ corresponds, as usual to the time of commencement of irradiation of the air in flask (2). The nucleus concentration in flask (2) followed the usual pattern for the dynamic method, reaching a peak value of 60,000 per c.c. at $T = 7.0$ minutes, and then decaying to a steady state value.

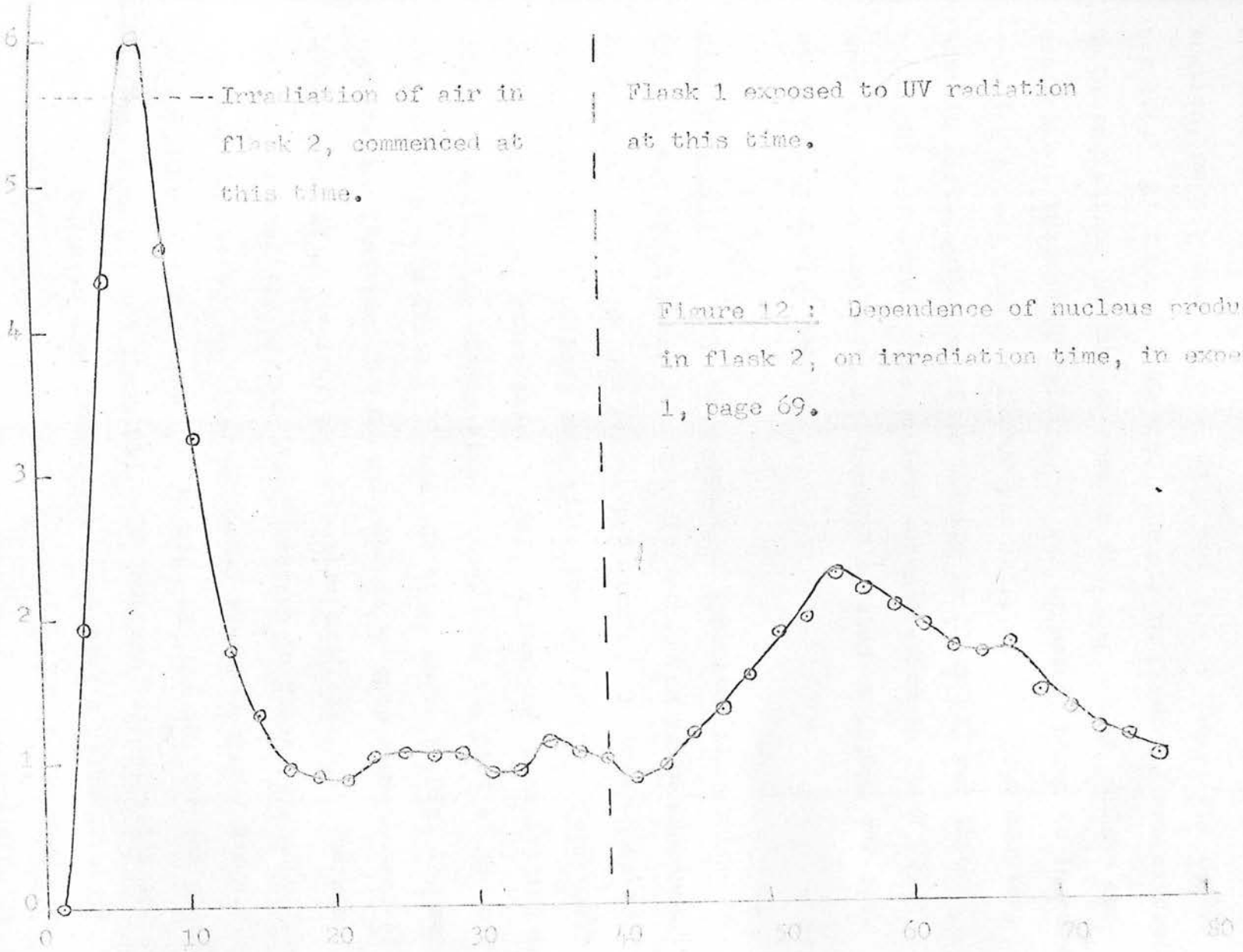


Figure 12 : Dependence of nucleus production in flask 2, on irradiation time, in experiment 1, page 69.

The mean value of the six measurements of steady state concentration, made between T = 29 min. and T = 39 min., was 10,200 per c.c. At time T = 40 min., the air in flask (1) was exposed to UV radiation. As may be seen in Fig. 12, the UV nucleus concentration, instead of falling, as was expected, began to increase, reaching a peak value of 22,800 per c.c., at T = 55.0 minutes, that is fifteen minutes after the air in flask (1) was exposed to the UV radiation. The nucleus concentration in flask (2) dropped, after the peak, and reached a value of 10,000 per c.c. at T = 1 hour 17.0 minutes.

Experiment (2): The arrangement of apparatus illustrated in Fig. 11 was again used. The dynamic method was again employed, at an airflow rate of 3.0 litres per minute. On this occasion, both flasks had been left exposed to the UV radiation from their respective lamps, overnight, so that the nucleus concentration in flask (2) was at its steady state value, when the plot of nucleus concentration (in flask (2)) against time, shown in Fig. 13, was commenced. The time T = 0 corresponds to this commencement of measurement of UV nucleus concentration in flask (2). The six measurements of the nucleus concentration in flask (2), made from T = 9.0 minutes to T = 19.0 minutes, averaged 49,000 per c.c. At the time T = 20.0 minutes in Fig. 13, the shutter was placed between lamp (1) and flask (1). The nucleus concentration in flask (2) began to drop immediately, reaching a value of about 11,000 per c.c., 31.0 minutes later, at T = 51.0 minutes. It remained almost constant at about this value until the time T was 1 hour 20 minutes. At this time, the shutter between lamp (1)

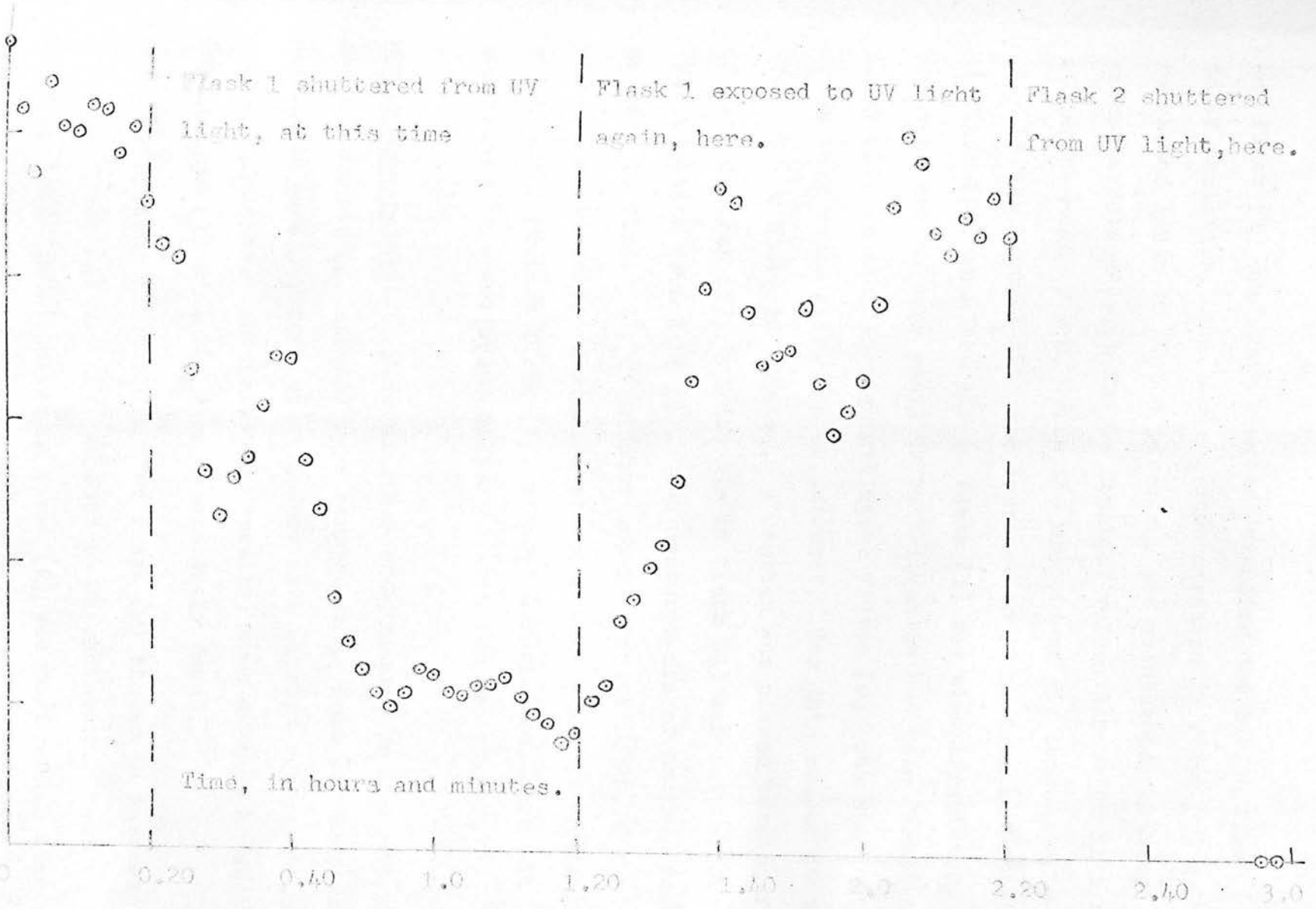


Figure 13 : Dependence of nucleus production in flask 2 , on time, in experiment 2, page 20

and flask (1) was again removed, exposing the air in flask (1) to UV radiation. The nucleus concentration in flask (2) rapidly increased again to 47,000 per c.c., and maintained, although rather erratically, a fairly constant value, almost as high as it had been at T = 0, when the experiment was commenced.

It was thought that the increase in UV nucleus concentration in flask (2), when the air in flask (1) was also irradiated, might be due to very small UV nuclei, which had been formed in flask (1), passing through Millipore filter (2) into flask (2) where they would grow, and be detected. For this reason at the time T = 2 hours 20 minutes, a shutter was placed between flask (2) and UV lamp (2), but the air in flask (1) was left exposed to the radiation from lamp (1). Two measurements of nucleus concentration in flask (2), 25 minutes and 27 minutes later, showed it had fallen to zero. Therefore it seems that small UV nuclei, which could grow in flask (2), without irradiation, were not penetrating the Millipore filter between the two flasks.

Other Experiments: Several other experiments, on the same lines as experiments (1) and (2) were carried out. Some of these experiments were carried out at a very slow airflow rate, of 0.5 litre per minute. the following results, some of them noted in experiments (1) and (2), were consistently found.

(A) UV nucleus concentration in flask (2) showed an increase, whenever flask (1) was also exposed to UV radiation. This increase in UV nucleus concentration in flask (2) was more marked when the rate of airflowwas 3.0 litres per minute, than when it was 0.5

litre per minute. At the airflow rate of 0.5 litre per minute, this increase was small enough to be within the limits of experimental error. An interesting feature of the increase in nucleus concentration in flask (2), on irradiation of the air in flask (1), was that the increase reached a peak value, and then decayed again to a lower, almost constant, value.

(B) In several other experiments, both flasks had been irradiated for a long time, so that nucleus concentration in flask (2) had reached a steady-state value; when a shutter was now placed between flask (1) and lamp (1), the nucleus concentration in flask (2) decreased rapidly, and remained at a lower value. This effect was also more marked at an airflow rate of 3.0 litres per minute, than at an airflow rate of 0.5 litre per minute.

Comparison of results with those of Hoppe:

As has been mentioned, the results found in these experiments were generally contrary to the expected results. It had been expected that UV nucleus concentration in flask (2) would show a drop when the air in flask (1) was also irradiated, due to the partial consumption of the trace gas or vapour assumed to be responsible for UV nucleus formation, on passing through flask (1). In fact the opposite occurred, and an increase in nucleus concentration in flask (2) resulted.

Walter Hoppe[31] was found to have carried out an almost similar experiment. He used two irradiation tubes of unspecified dimensions, instead of the author's two borosilicate flasks. He

used an airflow rate of 0.5 litres per minute, but because of the lack of values for the dimensions of the irradiation tubes, it is impossible to say what the residence times of the air in the tubes were. He irradiated the air with ultraviolet radiation of wavelengths as low as 2000 A. Also, in Hoppe's experiment the atmospheric air after passing through filter (1), irradiation tube (1) and filter (2), passed through a moistening tube first, before passing through irradiation tube (2).

Hoppe found that when he irradiated the air in irradiation tube (1), as well as irradiation tube (2), that the UV nucleus concentration in irradiation tube (2) dropped from 47,000 per c.c. to 20,000 per c.c., and remained at this value until the irradiation of the air in irradiation tube (1) ceased, when it increased again to 34,000 per c.c. Thus Hoppe found the kind of result that the author expected, whereas the author found the opposite. However, as has been mentioned, when an airflow rate of 0.5 litre per minute had been used by the author, these contrary results were not at all as marked.

Experiment 3: In order to make the author's experimental arrangement more like that of Hoppe, the humidifying tube, previously described, was placed in the air line between filter (2) and flask (2). With this arrangement of apparatus, using the dynamic method at an airflow rate of 3.0 litres per minute, the plot of UV nucleus concentration, in flask (2), against time shown in Fig. 14, was found. At time T = 0, UV nucleus concentration in flask (2)

Flask 1 exposed to the UV light at this time.

Figure 14 : Dependance of nucleus production in flask 2 on time, in exneriment 3, page 73.

was at the steady state value. At time T = 12.0 minutes, the air in flask (1) was also irradiated with ultraviolet light. UV nucleus concentration in flask (2), showed a temporary fall immediately, from about 700 per c.c. to 575 per c.c. This result is in agreement with Hoppe's results, but unfortunately it is not very reliable, as the rate of production of UV nuclei was very low and variable. Further experiments to confirm this result were not possible, since UV nucleus production in Millipore filtered air became very low, due to the outdoor air being usually clean, as a result of high winds at this time of the year. Passing the air through the humidifying tube between the two flasks, further reduced UV nucleus formation.

Discussion of Results:

The following observed results have to be explained.

(1) UV nucleus concentration in flask (2) increases, when the air in flask (1) is also irradiated, at an airflow rate of 3.0 litres per minute. This increase reaches a peak value, and then falls to a steady value.

(2) This increase is much less marked, at an airflow rate of 0.5 litre per minute.

(3) When a humidifying tube is placed between the flasks, as well as the Millipore filter, there seems to be a decrease in nucleus concentration in flask (2), when the air in flask (1) is also irradiated, the airflow rate being 3.0 litres per minute.

According to the trace gas hypothesis, some of the trace gas of vapour X, assumed to be responsible for UV nucleus formation, is consumed in flask (1), when irradiated, in the photochemical

reaction leading to the formation of nucleogenic substance Y. A fraction of Y is used to form nuclei in flask (1), but some of it remains in the gaseous state and passes from flask (1) into flask (2), through the Millipore filter, to add to the amount of Y produced photochemically there. Therefore, when flask (1) is irradiated, with flask (2) already being irradiated, two factors affect the nucleus formation in flask (2).

(A) The reduction in the concentration of X, due to consumption in flask (1), tends to reduce nucleus production in flask (2).

(B) The increase in the concentration of Y in flask (2), due to some of Y coming from flask (1), tends to increase nucleus production in flask (2).

At an airflow rate of 3.0 litres per minute, result (1) shows that there is an increase in nucleus production in flask (2) when the air in flask (1) is also irradiated, so that in this case factor (B) is dominant. The occurrence of a peak in this increase would be expected, since the amount of Y produced in flask (1) should show a similar peak, under the chemical super-saturation theory, when irradiation is commenced (see page (36)), and therefore the amount of Y passing to flask (2) should also show a similar pattern.

As the airflow rate is reduced to 0.5 litre per minute, the residence time of the air in the flasks increases. At this flow rate much more of X ought to be consumed, therefore, in flask (1), than was consumed at a flow rate of 3.0 litres per minute. However, although a corresponding increase occurs in the amount of Y produced in flask (1), the same increase will not apply to the

amount of Y passing from flask (1) to flask (2), since according to the chemical supersaturation hypothesis, a greater fraction of the Y produced in flask (1), is used up in forming nuclei, which are removed by the Millipore filter between the two flasks. The result is that factor (A) now almost balances factor (B), and there is only a small increase in nucleus production in flask (2), when flask (1) is also irradiated. It was not possible to use a smaller airflow rate than 0.5 litre per minute. If it had been, one would have expected to reach a critical airflow rate, where factor (A) became dominant, and there was a decrease in nucleus production in flask (2), when flask (1) was also irradiated.

In experiment (3), where a humidifying tube was placed in the air line, between the flasks, this decrease seemed to be already taking place, at an airflow of 3.0 litres per minute. This would be expected if Y is more soluble in water than X. This being the case a larger fraction of Y than of X, would be removed from the air passing from flask (1) to flask (2), by being dissolved in the water in the humidifying tube. The result would be that factor (A) would become dominant over factor B, at a higher rate of airflow. Thus it would be expected that a decrease in nucleus production in flask (2) when flask (1) was also irradiated, should occur at a higher rate of airflow, than when there is no moistening tube between the flasks. Result (3) shows that this in fact was the case.

It is of interest to note that such a result would be expected if the trace gas X is sulphur dioxide, and Y is sulphur trioxide (which leads to sulphuric acid formation, in the presence of water),

or sulphuric acid, since both these substances are much more soluble in water than sulphur dioxide.

These results therefore seem to be consistent with the trace gas hypothesis, and with the chemical supersaturation hypothesis.

An alternative hypothesis:

The only alternative hypothesis, which would explain results (1) and (2), is to assume that ultra-small nuclei are passed from flask (1) to flask (2), through the Millipore filter, and that these nuclei only grow to detectable size on irradiation in flask (2). It has already been shown, that small nuclei which grow to a detectable size without irradiation in flask (2), do not penetrate the Millipore filter. The smaller increase in nucleus production in result (2), would be due to fewer of these ultra-small nuclei penetrating the Millipore filter, at the slow airflow rate of 0.5 litre per minute. This hypothesis does not explain result (3). This hypothesis is not thought to be the correct one.

THE PRODUCTION OF UV NUCLEI IN CYLINDER GASES

The formation of nuclei in various cylinder gases, on UV irradiation, was now investigated. Since many of the trace gases and vapours present in city air would not be present in these cylinder gases, it would be informative to find out whether nuclei were in fact produced in these gases, on irradiation with ultra-violet light.

Argon was irradiated, first, in the borosilicate flask, using the static method, under the standard conditions. There was no need however for a pump, as the Argon was passed straight from a cylinder with a pressure reduction and regulating head, into the flask. No nuclei were produced in the Argon, even after a one hour static irradiation.

After this experiment had been carried out, it was found that no nuclei were produced, when air dried by silica gel or by a freeze-trap was used. It was thought that perhaps the reason why no nuclei were formed in the cylinder Argon on irradiation, was that there was not sufficient water vapour present in the gas. According to the suppliers of the Argon, there was less than 0.01 gm. of water per m^3 of gas, taken from a full cylinder. This water vapour content corresponds to less than 1% relative humidity at room temperature, so that the Argon was indeed very dry. For this reason it was decided to humidify cylinder gases for future irradiation.

The dynamic method of irradiation was used in these next experiments. The cylinder gas was passed from a cylinder, with a pressure reduction and regulating head, through the humidifying

tube previously used, into the flask. It could then pass through either the nucleus counter or the counter bypass tube, as usual. The gas flow rate was about 1.0 litre per minute, and was measured by a rotameter. The gases used were Argon, nitrogen and oxygen. No nuclei were detected in any of these gases, on irradiation. Table 3 shows the impurities present in these gases, according to the manufacturers.

Results of other workers:

There is great disagreement in the literature about the gases in which nuclei are produced, on irradiation with ultraviolet light.

Mulcahy and Kuffel[29] found similar, copious UV nucleus production in moist air and in moist Argon. Verzar and Kunz[24] found UV nucleus production in cylinder nitrogen. Saltmarsh[17] was able to produce large numbers of UV nuclei in carbon dioxide, but found little production in hydrogen, or in oxygen free nitrogen. Hoppe[31] produced many UV nuclei in air, oxygen and nitrogen, a few nuclei in Argon, and none in hydrogen. Vassails[27] found that many nuclei were produced in oxygen, carbon dioxide and hydrogen.

Many of these disagreements are due to the various experimental techniques used. Ultraviolet light of various wavelength distribution and intensity was used. The material of irradiation chambers may have caused UV nucleus formation in some cases. Cotton wool filters were used, often, for various gases, and as the author found out, these filters can contaminate gases passing through them.

TABLE 3

Gas	A	O_2	N_2	H_2	Ne
Argon	more than 99.95°/o	less than 10 PPM	less than 500 PPM	less than 1 PPM	
Nitrogen	less than 50 PPM	0.05°/o	99.9°/o	about 20 PPM	about 600 PPM
Oxygen	less than 0.5°/o	more than 99.5°/o	less than 0.1°/o	less than 50 PPM	-

Gas	He	CO_2	Carbonaceous as CO_2	H_2O vapour
Argon	-	less than 5 PPM	less than	For full cylinder less than 0.01 gm/m^3.
Nitrogen	about 160 PPM	less than 20 PPM	less than 5 PPM	For full cylinder about 0.05 gm/m^3
Oxygen	-	less than 5 PPM	less than 25 PPM	less than 200 PPM or 0.05 gm/m^3

Discussion of results:

It seems from the author's results that UV irradiation of Argon, nitrogen or oxygen, with admixture of impurities listed in Table 3, does not lead to nucleus formation, with ultraviolet light of wavelength greater than 2900A. The passage of these gases through a humidifying tube should not completely remove their UV nucleus forming power, if they had any, as it did not do so with the atmospheric air used in previous experiments. Consequently the trace gas or vapour X responsible for UV nucleus formation in city air, must be one of those trace gases present in city air, but missing, in sufficient quantity, from these cylinder gases.

UV NUCLEUS PRODUCTION IN ROOM AIR AND IN OUTDOOR AIR COMPARED:

In one experiment the dynamic method was used to compare UV nucleus production in room air and in outdoor air. It was expected that UV nucleus production would be higher in outdoor air, since outdoor city air generally contains a higher concentration of trace gases such as sulphur dioxide, than does room air. Outdoor air, filtered through a Millipore filter was first used, at an airflow rate of 3.0 litres per minute. The steady state UV nucleus concentration reached was about 530 per c.c., which is the mean of the last four measurements made, before using room air. The room air was now drawn in through the Millipore filter, instead of outdoor air, by disconnecting the filter from the inlet tube for outdoor air, which passed through a hole in the top of a window frame. UV nucleus concentration in the flask began to drop, and

reached a steady value of about 85 per c.c. some 20 minutes after beginning to use room air. Outdoor air was now used again, and UV nucleus concentration in the flask increased again, the mean value of 3 measurements 30 minutes later being 330 per c.c. Thus it seemed indeed that more UV nuclei were produced in outdoor air than in room air. Further experiments confirmed this result. Therefore it seems that the trace gas or vapour X responsible for UV nucleus formation, is present at a higher concentration in outdoor air than in room air.

EVIDENCE THAT UV NUCLEI ARE PRODUCED IN THE IRRADIATED AIR IN THE FLASK, AND NOT BY THE ADIABATIC EXPANSION IN THE COUNTER.

It has been suggested by some workers such as Evans and Watson[28] and Dunham[46], that nuclei produced from trace impurities in air, may not be formed until an adiabatic expansion is made in a cloud chamber or nucleus counter. It seemed possible therefore that the UV nuclei, which are assumed to be formed from a photochemical reaction product Y, might not be produced in the air in the flask, on irradiation, but might instead be formed when an adiabatic expansion was made in the nucleus counter. In order to investigate this hypothesis, a Millipore filter of pore size 1.2 micron, was placed in the air line between the borosilicate flask and the nucleus counter. As was mentioned earlier, this filter holds back nuclei much smaller in diameter than 1.2 micron, due to the build up of electrostatic charge on the filter. If nuclei were produced by the expansion in the nucleus counter, or by the reaction or condensation of gaseous products, after leaving the flask, nuclei should still be detected by the Nolan-Pollak counter, with the Millipore

filter placed in the air line between the flask and the counter. According to Junge[51], a new Millipore filter absorbs up to 50°/o of trace gases ammonia and chloride, and less than 50°/o of sulphur dioxide and nitrogen oxide. However this effect decreases with time, and is not significant for filters which have been in use for some time. For this reason, the Millipore filter used in these experiments had already been used for at least one hour.

No nuclei were detected in the counter, after a 6.0 minute static irradiation of filtered outdoor air in the flask although when the filter was not in the air line between the flask and the counter, a concentration of nuclei, of the order of 280,000 per c.c. was measured by the counter. The filter therefore removed these nuclei from the air. Similarly the nuclei existing at various irradiation times, when the dynamic method was used, were removed completely by the Millipore filter.

Therefore it seems that the UV nuclei are produced in the irradiated air in the flask, and not by the subsequent condensation or reaction of gaseous products, or by the adiabatic expansion in the nucleus counter.

THE UV NUCLEUS PRODUCTION IN AIR ALREADY CONTAINING NUCLEI.

It was now decided to irradiate air containing nuclei, in order to find out if the existence of nuclei in the air, before irradiation, had any effect on the number of new nuclei detected after irradiation.

The static method of irradiation was used, and all air samples were irradiated for a time of 6.0 minutes. The concentration of nuclei in the flask before irradiation, Z_T, was measured 2.0 minutes before irradiation commenced, as usual. Outdoor air filtered through cotton wool was used for the first 6.0 minute irradiation, and as would be expected, Z_T in this case was zero. Air containing various concentrations of nuclei, Z_T, was obtained for the other 6.0 minute irradiations by using unfiltered outdoor air, (Z_T = 43,800; 53,800), unfiltered room air (Z_T = 28,300), and outdoor air which was inefficiently filtered through a 1.2 micron pore size Millipore filter. All the irradiations were carried out on the same afternoon, so that the outdoor air used in the various experiments ought to have been similar in quality, except for condensation nucleus content.

Table 4 shows the concentration Z_T of nuclei existing in the air two minutes before irradiation, and the corresponding concentration Z of new nuclei detected in that air after a 6.0 minutes static irradiation. Z is the actual concentration of nuclei actually measured, after irradiation, less Z_T.

TABLE 4

Nucleus concentration before irradiation	Concentration of new nuclei produced
Z_T in nuclei per c.c.	Z in nuclei per c.c.
0	285,000
1,500	189,000
28,300	127,000
43,800	37,100
53,800	71,000

Discussion of Results:

It seems from the results of this experiment, in Table 4, that generally the greater the number of atmospheric nuclei present in the air, on irradiation, the fewer new nuclei are produced by the irradiation.

O'Connor[36], when investigating the production of condensation nuclei by UV radiation in a borosilicate flask containing decaying seaweed and air, found that very few new nuclei were produced by UV irradiation, if nuclei at a concentration in excess of 1,000 per c.c., already existed in the air in the flask, at the commencement of irradiation. However if there were no nuclei, or very few nuclei present in the air on irradiation, then large numbers of nuclei were produced. His findings support the author's results. O'Connor proposed that the nuclei were produced by the irradiation of some gas emanating from the decaying seaweed, and

that "in the presence of nuclei, some of this gas was possibly absorbed on the nuclei, so that it did not form new nuclei."

As was mentioned earlier in this work, Goetz and Kallai[48] found that latex nuclei present in air on UV irradiation, grew to a larger size when the air was irradiated, than when no irradiation occurred, probably due to the condensing on them of some photochemical reaction product. They also noticed that whenever an "insufficient" number of nuclei existed in the irradiated air, some new particles, very small, and of a different constitution to the latex nuclei, were produced on UV irradiation. Similar results were also reported by Goetz and Pueschel,[49] who found that a higher concentration of nuclei were produced by irradiation of a mixture of nitrogen dioxide and octene-I in air, when no nuclei already existed in the gas on irradiation, than if such nuclei existed. When nuclei already existed in the gas on irradiation, the nucleogenic substance which was produced in the gas photochemically, condensed on the existing nuclei to a large extent, and formed relatively few new nuclei.

There is a good deal of support for the author's results, therefore, in the literature. The author's results also support the chemical supersaturation hypothesis. When nuclei are already present in the air on UV irradiation, the average chemical supersaturation of the gas, with nucleogenic substance Y, can not rise as high as it would with no nuclei present. This is so, because Y begins to condense on the nuclei already present in the gas. Therefore, less of Y is available for the formation of new nuclei, and so, less new nuclei are produced. The greater the

number of nuclei present in the gas on irradiation, the greater the fraction of Y condensing on existing nuclei, and therefore the least new nuclei produced. Thus the results expected according to the chemical supersaturation hypothesis, are qualitatively similar to those found in the author's experiments.

The author's results do not support the hypothesis that the reason why fewer new UV nuclei are produced in the air when nuclei already exist in the gas on commencement of irradiation, is that the trace gas or vapour X assumed to be responsible for UV nucleus formation is absorbed by existing nuclei. If the atmospheric nuclei, which were present in the air, in the author's experiment, at the commencement of irradiation, can absorb trace gas or vapour X, they would have done so long before the experiment, as they co-existed with X in the atmospheric air used.

DEPENDENCE OF UV NUCLEUS PRODUCTION IN THE DYNAMIC METHOD ON THE RATE OF AIRFLOW

It would be interesting to investigate the dependence of U-V nucleus formation in filtered air, on the intensity of the ultraviolet radiation used. However, with the arrangement of apparatus used in this work, the intensity of the ultraviolet radiation varied significantly from point to point inside the flask (see page 165). Therefore it was considered that an experiment in which the intensity of the UV light, irradiating the flask, was varied, would not be very informative.

It was decided instead, to vary the rate of airflow through the flask, from one experiment to the next, employing the dynamic method. In this way the average amount of ultraviolet light energy received by a unit volume of the air would also be varied, since this is proportional to the average residence time of a unit volume of air in the flask; which in turn is inversely proportional to the rate of airflow through the flask.

Experimental Procedure

The dynamic experiment was carried out several times, using a different fixed rate of airflow each time. The rate of airflow used, varied from 1.5 litre per minute to 10 litres per minute, from experiment to experiment. Outdoor air, filtered through cotton wool, was used in all the experiments, which were carried out over a period of three consecutive days. A lower rate of airflow than 1.5 litre per minute was not used, since a long delay

would have ensued between the time of production of nuclei, in the flask, and the measurement of their concentrations in the counter, under such conditions. Rates of flow in excess of 10 litres per minute were not used, since nuclei were not produced in the dynamic experiment, at such airflow rates. Before the commencement of irradiation in each experiment, the flask was flushed with freshly filtered air, for a sufficient time to flush the flask with about ten times its volume of this air. In each experiment, measurements of nucleus concentration were made at two minute intervals, the first irradiated air sample being isolated in the nucleus counter, one minute after commencement of irradiation.

Results:

The results of this series of experiments, are presented in tabular form in Table 5. L is the rate of airflow in litres per minute. T_{max} is the time from the commencement of irradiation to the occurrence of maximum nucleus concentration. This is taken to be the time after commencement of irradiation, at which the air sample containing maximum measured nucleus concentration, was isolated in the nucleus counter. Z_{max} is the maximum nucleus concentration measured for each airflow rate. Z is the mean of the last six measurements of nucleus concentration in each hour long experiment. This is in other words the steady-state UV nucleus concentration, as the concentration had reached its steady state value by this time, for all rates of airflow.

TABLE 5

The dependence of UV nucleus production on airflow rate in the dynamic method.

L in litres/min.	T_{max} in minutes	Z_{max} in nuclei/c.c.	Z in nuclei/c.c.	Z_{max}/Z
1.5	7.0	215,000	60,500	3.6
2.0	7.0	238,000	50,800	4.7
3.0	7.0	144,000	38,800	3.7
4.0	7.0	59,300	12,000	5.0
5.0	5.0	33,000	8,410	3.9
6.0	5.0	24,100	4,770	5.1
7.0	5.0	1,980	958	2.1
8.0	5.0	580	118	4.9
9.0	5.0	234	95	2.5
10.0	5.0	61	5	12.2

Finally, the table gives Z_{max}/Z, the ratio of maximum UV nucleus concentration to steady state concentration.

The concentration of nuclei decreased, as would be expected, with increasing airflow rate. There is one exception, as Z_{max} for an airflow rate of 1.5 litres per minute is less than the Z_{max} for 2.0 litres per minute. This is so, probably, because the measurement of Z_{max} at the very slow airflow rate of 1.5 litres per minute, was not very accurate, due to the delay in getting the air sample from the flask to the counter, thus allowing mixing with air containing less nuclei, during this delay. The maximum nucleus concentration had decreased to an almost negligible 61 per c.c. at an airflow rate of 10.0 litres per minute. Z showed a similar decline with increasing airflow rate, and was only an insignificant 5 per c.c. at L = 10 litres per minute. The time of occurrence of Z_{maz} was 7.0 minutes for all airflows from 1.5 to 4.0 litres per minute, inclusive, and 5.0 minutes for all airflows from 5.0 to 10.0 litres per minute, inclusive, thus showing remarkable consistency.

The ratio Z_{max}/Z was fairly constant, having a value within the range 3.6 to 5.1, for airflow rates up to and including 6.0 litres per minute. It dropped as low as 2.1 at an airflow rate of 7.0 litres per minute. The value of 12.2 for an airflow rate of 10.0 litres per minute, is unreliable as counter measurements of the small nucleus concentrations for this airflow rate are inaccurate.

Discussion of Results:

In Fig. 15, a plot of $\log_{10} Z_{max}$ against $\log_{10} L$, and a plot of $\log_{10} Z$ against $\log_{10} L$ are shown. The plot in both cases is nearly a straight line of slope -2, for airflows from 1.5 to 6.0 litres per minute, remembering that the values of Z_{max} and Z for $L = 1.5$ litres per minute, are probably too low. For airflow rates from 7.0 to 10.0 litres per minute, the plots do not follow this straight line. There is a sort of knee on both plots between $L = 6.0$ litres per minute and $L = 7.0$ litres per minute. This is significant, because as was mentioned earlier the ratio Z_{max}/Z remained almost constant from $L = 1.5$ litres per minute to $L = 6.0$ litres per minute, and showed a wider variation for higher air flows.

Let us therefore make the reasonable assumption that the plot of $\log_{10} Z$ (or $\log_{10} Z_{max}$) against $\log_{10} L$ is a straight line of slope -2. This gives a relationship between Z and L of the form

$$\log_{10} Z = A - 2 \log_{10} L \qquad (1)$$

where A is a constant.

The form of the equation may be changed to

$$\log_{10} Z = 2 \log_{10} A' - 2 \log L$$

where A' is another constant.

$$\text{Thus, } \log_{10} Z = 2 \log \frac{A'}{L}$$

$$\text{or } Z = \frac{K}{L^2} \qquad (2)$$

where K is a constant.

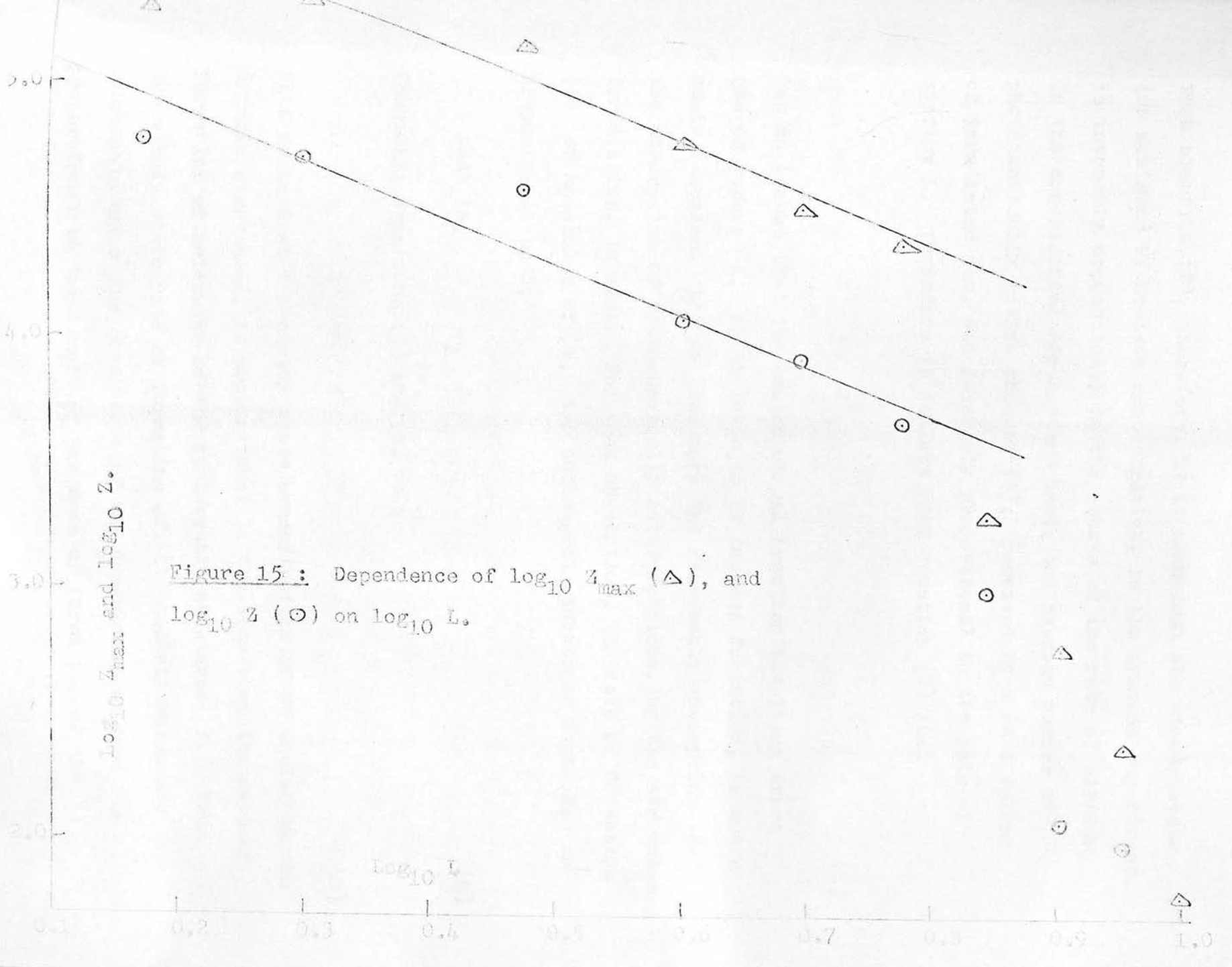


Figure 15 : Dependence of $\log_{10} Z_{max}$ (△), and $\log_{10} Z$ (⊙) on $\log_{10} L$.

From equation (2), therefore, it is seen that the steady state (or maximum) UV nucleus concentration, in the dynamic experiment, is inversely proportional to the square of the rate of airflow. In the experimental arrangement used, the average number of photochemically active photons (J), received by a unit volume of irradiated gas, was inversely proportional to the rate of airflow L. Therefore it follows from equation (2) that

$$Z \propto J^2 \qquad (3)$$

Let us assume that the photochemical reaction involving trace gas or vapour X, which leads to UV nucleus formation, is not a chain reaction. Let us also make the reasonable assumption that the absorption of photochemically active photons, by the air under irradiation, is weak. For weak absorption, the rate of formation (F) of molecules of Y, the nucleogenic substance from X, is proportional to J,

$$\text{that is,} \quad F \propto J \qquad (4)$$

Combining equations (3) and (4) we get

$$Z \propto F^2 \qquad (5)$$

This means that the steady state concentration of UV nuclei in the dynamic experiment, is proportional to the square of the rate of formation of molecules of the nucleogenic substance Y. Thus the steady state rate of formation of UV nuclei, which are detectable under the conditions of the dynamic experiment, is proportional to the square of the rate of formation of the

nucleogenic substance Y, if the assumptions made by the author are correct.

Agreement of results with those of other workers:

Hoppe[31] added definite small amounts of sulphur dioxide to atmospheric air, and found that the concentration of condensation nuclei produced on UV irradiation, was proportional to the square of the sulphur dioxide concentration. Leighton[45] states that the nuclei formed by UV irradiation of sulphur dioxide in air of normal humidity, have been shown to be droplets of moderately dilute sulphuric acid (about 43°/o sulphuric acid, at 50°/o relative humidity). Hall[53] found that the rate of formation of sulphuric acid molecules, during irradiation of sulphur dioxide and oxygen mixtures, was directly proportional to the sulphur dioxide concentration. If the assumptions made are the correct ones, the experimental results of these workers suggest that the rate of formation of sulphuric acid nuclei during UV irradiation of low concentrations of sulphur dioxide in air, is proportional to the square of the rate of formation of sulphuric acid molecules. This deduction is therefore similar to the conclusion based on the results of the author's experiment, that is, that the rate of formation of UV nuclei, which are detectable under the conditions of the dynamic experiment, is proportional to the square of the rate of formation of the nucleogenic substance Y .

The agreement of these conclusions does not necessarily mean that the UV nuclei detected in the author's experiments are moderately dilute sulphuric acid droplets, produced as a result of the UV irradiation of sulphur dioxide in the filtered air; in

other words that the author's trace gas or vapour X is sulphur dioxide, and that the photochemical reaction product Y is sulphuric acid. It may be a general law, that the rate of formation of condensation nuclei from molecules of a nucleogenic reaction product, being produced at a steady rate, as in a normal photochemical gaseous reaction, is proportional to the square of the rate of formation of molecules of that reaction product. However, it is interesting that according to these conclusions, the trace gas or vapour X, assumed to be responsible for UV nucleus formation in city air, could be sulphur dioxide.

Agreement with theory:

Dunham[46] produced a theory for the formation of condensation nuclei, as a result of homogeneous nucleation, due to chemical supersaturation. As was mentioned on page 39 of this work, Dunham solved equations derived from a consideration of the Becker-Doring theory of homogeneous nucleation, and the Mason theory of droplet growth, for a system where a nucleating substance is being produced at a constant rate, as in a photochemical reaction. With sulphuric acid as the nucleating substance, his theory suggested that the rate of formation of sulphuric acid nuclei, should be proportional to the $I^{3}/8$th power of the rate of formation of sulphuric acid molecules. This theory is not in agreement with the conclusions drawn from the experiments of Hoppe and Hall, that the rate of formation of sulphuric acid (moderately dilute) nuclei is proportional to the square of the rate of formation of sulphuric acid molecules. However, Dunham assumed "that the

mechanism by which the particles grow is by the addition of nucleating substance molecule by molecule." Thus, it seems that he considered the growth of sulphuric acid nuclei to take place by addition of sulphuric acid molecules only. Therefore his theory can not be applied to the problem of the formation of sulphuric acid (moderately dilute) nuclei, during the ultra-violet irradiation of the sulphur dioxide present in atmospheric air, since the nuclei in this case would also grow by addition of water molecules, and perhaps by addition of molecules of other trace substances. Sulphuric acid, when concentrated, avidly attracts water molecules, and there are always far more water molecules, than sulphur dioxide molecules, present in atmospheric air.

Discussion of the times of occurrence of peak nucleus concentrations, for different rates of airflow:

Peak nucleus concentration occurred for airflow rates from 1.5 to 4.0 litres per minute, inclusive, 7.0 minutes after commencement of irradiation. It occurred 5.0 minutes after commencement of irradiation for airflow rates from 5.0 to 10.0 litres per minute, inclusive. The change of T_{max} from 7.0 minutes to the earlier occurrence, at the higher rates of airflow may be simply due to the fact that nuclei formed at a particular time in the flask, reach the counter more quickly, at the higher rates of airflow. It must be remembered that measurements of nucleus concentration were only made at two minute intervals, so that it was not possible to get a more accurate value for T_{max}. It seems

therefore that T_{max} remained almost constant, for all rates of airflow.

Agreement of this result with the chemical supersaturation hypothesis:

According to the chemical supersaturation hypothesis, substantial production of UV nuclei should occur when a certain critical supersaturation S^X of the air, with the photochemical reaction product Y is achieved. A "time delay" with little or no nucleus production should occur, after commencement of irradiation, while this critical supersaturation of the air with Y is building up. Therefore according to the chemical supersaturation hypothesis, as the rate of airflow is increased, it should take a longer time for the critical supersaturation S^X to be built up, as the molecules of Y formed, are distributed throughout a greater volume of air. Therefore, one would expect "the time delay" to increase, as the airflow rate increases. In the author's experiments, the "time delay" did not vary within the limits of experimental error, with the rate of airflow. Similarly, according to the chemical supersaturation hypothesis, it seems that T_{max} should increase as the rate of airflow increases. As was mentioned earlier, this was not the case, in the author's experiments, as T_{max} remained almost constant.

The results of this experiment, therefore, do not seem to support the chemical supersaturation hypothesis, although this hypothesis was capable of explaining qualitatively the pattern of UV nucleus production, in air, at a given flow rate.

Agreement of results with hypothesis that peak nucleus concentration is due to nuclei being emitted from flask wall:

This hypothesis was mentioned earlier in this work. It suggests that the peak nucleus concentration, observed in the static and dynamic experiments, is due to a transient production of nuclei, or nucleogenic material, which is emitted from the inside glass walls of the borosilicate flask, on irradiation, due to the occlusion of impurities on the glass surface.

The author's result that T_{max} remained almost constant for all rates of airflow used, would tend to support this hypothesis, since the time of occurrence of maximum concentration, for nuclei emitted from a surface, should be independent of the rate of airflow.

On the other hand, the surface area from which the nuclei are emitted, according to this hypothesis, remains constant, as the rate of airflow is changed. Therefore, the time rate of formation of such nuclei should remain constant, so that peak nucleus concentration should be inversely proportional to the rate of airflow L. In the author's experiment, peak nucleus concentration seemed to be inversely proportional to the square of the rate of airflow. This result, then, does not support the above hypothesis.

Agreement of results with hypothesis that occurrence of peak nucleus concentration is due to the absorption of trace gas X by existing nuclei:

This hypothesis, also mentioned already (see page 44) suggests that the occurrence of peak nucleus concentration is due to the absorption of trace gas X by existing nuclei, so that the amount

of X available for the production of new nuclei is depleted. In the dynamic experiment, the concentration of X in the air should be almost independent of the rate of airflow, for the rates of airflow used in the author's experiment, since it has been shown in previous experiments that X is consumed very slowly in the flask. The concentration of nuclei produced using a high rate of airflow was smaller than the concentration produced using a slow rate of airflow. The relatively few nuclei present in unit volume of the air, at the higher rate of airflow, should take a longer time to absorb a given fraction of trace gas or vapour X, than the relatively large number of nuclei present in a unit volume of air, at the low airflow, do. Therefore, either

(A) T_{max} should increase as the rate of airflow increases

or

(B) The ratio Z_{max}/Z should decrease as the rate of airflow increases.

Neither (A) nor (B) was observed to occur in the author's experiment; therefore the above hypothesis is not favoured.

Agreement of results with hypothesis that occurrence of peak nucleus concentration is due to coagulation of new nuclei with existing nuclei:

This hypothesis was also mentioned earlier in this work. It suggests that the occurrence of peak nucleus concentration is due to the coagulation of the very small new nuclei with existing nuclei (see page 43). It is shown by the author later in this work that the great majority of UV nuclei detected in the counter are

uncharged nuclei. The rate of coagulation of uncharged nuclei of given radius, is approximately proportional to the square of the nucleus concentration. Therefore, the rate of mutual coagulation should have been much smaller in the author's experiments, when the airflow rate was fast, than when it was relatively slow, since there was a much smaller UV nucleus concentration in the air then. For this reason, T_{max} ought to increase significantly with increasing rate of airflow, according to the above hypothesis, since it would take a longer time, at the small nucleus concentration then existing, for the rate of loss of all existing nuclei, to become greater than the rate of formation of new nuclei, which remain uncombined with existing nuclei. However, T_{max} was observed to remain almost constant, as the rate of airflow was increased, so that the author's experimental results do not support the above hypothesis.

The results of the above experiments therefore do not seem to support any of the hypotheses discussed so far in this work, to explain the occurrence of peak nucleus concentration in the dynamic method, and no satisfactory alternative hypothesis is available.

THE MEASUREMENTS OF THE SIZES OF UV NUCLEI

It was decided to attempt to measure the sizes of the UV nuclei produced in the air in the flask. These nuclei can not be made directly visible in the ultramicroscope, and they are not numerous enough to produce an observable amount of light scattering. Therefore, the method normally used for the determination of the size of condensation nuclei, involves the measurement of the coefficient of diffusion of these nuclei in the gas in which they are suspended.

There are two main experimental methods used for determining the "diffusion coefficient" (shortly to be defined), of nuclei. One method, developed by Nolan J.J. and Guerrini (1935)[53], and Nolan J.J. and Nolan P.J. and Gormley (1938)[54] is called the dynamic method. The second method, called the static method, was developed by Pollak, O'Connor and Metnieks (1956)[55], and is based on the theory developed by Fürth[56]. Since only one nucleus counter was at the author's disposal, it was considered that the use of either of the two above mentioned methods was inadvisable, because:

(1) When air filtered through cotton wool was used, the steady state nucleus concentration in the dynamic method of irradiation, was normally of the order of 40,000 per c.c., which is too high for the satisfactory use of either of these two methods.

(2) When air filtered through a Millipore filter was used, the steady state nucleus concentration in the dynamic method of irradiation was often of the right order of magnitude, for these two methods, but it was too variable, with time.

It was decided to try a method of size measurement, based on the measurement of the rate of mutual coagulation of nuclei produced

in the static method of irradiation of the air in the flask, the theory of which is outlined below.

(Note: Care must be taken not to confuse the static and dynamic methods of irradiation of the air in the flask, with the static and dynamic methods for the measurement of the diffusion coefficient of the nuclei.)

Theory of the method used for the measurement of the size of UV Nuclei:

The experiments of Kennedy[57] and Nolan[58,59], and Nolan and Kuffel[60], showed that the concentration of nuclei enclosed in a closed vessel, decreases with time, in accordance with the equation

$$-\frac{dZ}{dt} = \gamma Z^2 + \lambda Z \qquad (1)$$

where Z is the number of nuclei per c.c., t is the time, γ is the coagulation coefficient, and λ is a coefficient relating to loss by diffusion to the walls of the container, and by sedimentation to the floor of the container, under gravity.

$$\lambda = \lambda_d + \lambda_g \qquad (2)$$

where λ_d is the part of λ due to diffusion to the walls of the container, and λ_g is the part due to sedimentation.

Nolan and Kuffel stated the following equations, on the assumption that there exists sufficient mixing in the container, to keep the nucleus concentration uniform, except in a boundary layer, in which the gradient is uniform

$$\lambda_d = \frac{D}{a} \cdot \frac{A}{V} \qquad (3)$$

and $$\lambda_g = \frac{c}{h} \qquad (4)$$

where 'D' is the diffusion coefficient, 'a' the thickness of the boundary layer, 'c' the velocity of fall of the nuclei under gravity. The dimensions of the vessel are; A the inner surface area, V the volume, and h the height. It is assumed that the vessel has a uniform horizontal cross-section, in equation (4).

The diffusion coefficient D is defined, using Einstein's[61] equation, derived from his theory of Brownian movement:

$$D = k\,T\,B \qquad (5)$$

Here k is Boltzmann's constant, T the absolute temperature of the gas, assumed to be uniform throughout the vessel. B is the mobility for translational movement of the nuclei, and is defined by the equation

$$v = BF \qquad (6)$$

which relates the terminal velocity of a particle to a constant force F acting on it. B depends on the size and shape of the particle, and on certain molecular properties of the surrounding medium, but not on the material of the particle.

The force F experienced by a spherical particle of radius r, travelling at terminal velocity, in a gas, is given by the following modification of the Stokes-Cunningham[62] law, due to Millikan[63,64]

$$F = \frac{6\pi \eta r v}{1 + \frac{\ell}{r}(A + B' e^{\frac{-cr}{\ell}})} \qquad (7)$$

where η is the macroscopic viscosity of the gas, r the radius of the particle, v the terminal velocity of the particle. ℓ is the mean free path of the gas molecules, as defined by the equation

$$\eta = 0.3502 \rho \bar{c} \ell \qquad (8)$$

where ρ is the density of the gas, $\bar{c}$ the mean thermal velocity of the gas molecules. A, B' and c are constants, whose values are given by Millikan as $A = 0.864$, $B' = 0.290$ and $c = 1.25$.

From equations (7) and (6) it is found that the mobility

$$B = \frac{1 + \frac{\ell}{r}(A + B' e^{\frac{-cr}{\ell}})}{6\pi\eta r} \qquad (9)$$

Therefore, from equation (5) it follows that the diffusion coefficient

$$D = \frac{kT}{6\pi\eta} \cdot \frac{1 + \frac{\ell}{r}(A + B' e^{\frac{-cr}{\ell}})}{r} \qquad (10)$$

The assumption will be now made, that the radius of the particle, is much smaller than ℓ the mean free path of the gas molecules. The value of ℓ, at 15°C, as given by equation (8), is 9.06×10^{-6} cm. Equation (10) now simplifies to approximately

$$D = \frac{kT}{6\pi\eta} \cdot \frac{\ell(A + B')}{r^2} \qquad (11)$$

Using the values of the parameters, at 15°C and 760 mm. Hg. pressure, and substituting for the constants A and B', we find

$$D = \frac{1.24 \times 10^{-16}}{r^2} \quad ; \quad \text{for} \quad \ell >> r \qquad (12)$$

The coagulation coefficient γ, in equation (1) was derived theoretically by Smoluchowski[65], for coagulation of sols of uniform radii, to be

$$\gamma = 8\pi r D \qquad (13)$$

Nolan and Kennan[66] and Nolan and Kuffel[60] obtained a fair measure of agreement with equation (13), for small nuclei with r less than ℓ.

It is now assumed that the concentration of nuclei Z is sufficiently high and the dimensions of the vessel of such values as to make

$$\gamma Z^2 >> \lambda Z \quad , \qquad (14)$$

in equation (1), so that the fall in nucleus concentration due to mutual coagulation is much greater than the loss due to diffusion to the walls of the vessel and due to sedimentation. Equation (1) is now approximately

$$-\frac{dZ}{dt} = \gamma Z^2 \qquad (15)$$

From equations (13) and (15) we find

$$-\frac{dZ}{dt} = 8\pi r D Z^2 \qquad (16)$$

From equation (12) we have

$$D = \frac{K}{r^2} \quad , \quad \text{where} \quad K = 1.24 \times 10^{-16}$$

Substituting for D in equation (16), we have

$$-\frac{dZ}{dt} = \frac{8\pi KZ^2}{r} \qquad (17)$$

It is now assumed that an experiment of short duration is carried out; that Z_o and r_o respectively are the concentration of nuclei in the container and the radius of all the nuclei, respectively, at the commencement of the experiment; and that Z is the concentration, and r the corresponding radius, of nuclei, at the end of the experiment. The experiment is assumed to be of sufficiently short duration, that the loss of nuclei by diffusion to the walls of the container, and by sedimentation, is negligible. The total volume of nuclei per unit volume of gas, will then remain almost unaltered, so that, approximately,

$$Zr^3 = Z_o r_o^3 = \text{constant} \qquad (18)$$

Therefore, differentiating

$$\frac{d(Zr^3)}{dt} = 0$$

$$Z\frac{d(r^3)}{dt} + r^3\frac{dZ}{dt} = 0$$

Therefore

$$3r^2\frac{dr}{dt} \cdot Z + r^3\frac{dZ}{dt} = 0$$

so that $$-\frac{dZ}{dt} = \frac{3Z}{r} \cdot \frac{dr}{dt} \qquad (19)$$

Equating the value of $-\frac{dz}{dt}$ in equations (17) and (19), it is found that

$$\frac{3Z}{r} \cdot \frac{dr}{dt} = \frac{8\pi K Z^2}{r}$$

so that $$\frac{dr}{dt} = \frac{8\pi K}{3} \cdot Z \qquad (20)$$

Substituting for Z from equation (18)

$$\frac{dr}{dt} = \frac{8\pi K}{3} \cdot \frac{Z_o r_o^3}{r^3}$$

therefore $$r^3 \frac{dr}{dt} = \frac{8\pi K}{3} \cdot Z_o r_o^3 \cdot$$

Integrating $$r^4 = \frac{32\pi K}{3} \cdot Z_o r_o^3 t + C$$

where C is a constant.

Assuming that $r = r_o$ when $t = 0$, that is at the commencement of the experiment, we find $C = r_o^4$

so that $$r^4 = \frac{32\pi K}{3} \cdot Z_o r_o^3 t + r_o^4$$

or $$\left(\frac{r}{r_o}\right)^4 = \frac{32\pi K}{3} \cdot \frac{Z_o t}{r_o} + 1 \qquad (21)$$

From equation (18)

$$\left(\frac{r_o}{r}\right)^3 = \left(\frac{Z}{Z_o}\right)$$

or $$\left(\frac{r_o}{r}\right) = \left(\frac{Z}{Z_o}\right)^{1/3}$$

Substituting for $\frac{r}{r_o}$ in equation (21)

$$\left(\frac{Z_o}{Z}\right)^{4/3} = \frac{32\pi K}{3} \cdot \frac{Z_o t}{r_o} + 1 \qquad (22)$$

and substituting for π, and for K, the following relationship is found.

$$\left(\frac{Z_o}{Z}\right)^{4/3} = 4.155 \times 10^{-15} \cdot \frac{Z_o t}{r_o} + 1 \qquad (23)$$

If the value of Z_o, the concentration of nuclei at the commencement of the experiment is known, and the value of Z, the concentration of nuclei at a time t seconds later, then, equation (23) enables one to calculate r_o, the radius of the nuclei at the commencement of the experiment. The conditions laid down by the assumptions made, in deriving equation (23), must of course be fulfilled.

Experimental Procedure:

Outdoor air which had been filtered through cotton wool, was irradiated for 6.0 minutes, using the static method of irradiation. A small fraction of the irradiated air was then drawn through the nucleus counter, and a measurement of nucleus concentration made. The nuclei remaining in the flask were allowed to coagulate for a time t, before being sampled again. As the concentration of nuclei, in the air in the flask, before and after this coagulation period was known, it was possible to get a value for r_o, the radius of the nuclei, shortly after the completion of the irradiation. The arrangement of apparatus normally used for the static method of irradiation was employed. The detailed experimental procedure is given below. T is the time after commencement of the experiment.

T (mins. and secs.)

0.0 The flushing of the flask, with fresh filtered air was commenced.

15.0 The airflow was diverted from the counter bypass tube to the counter.

T (mins. and secs.)

16.0 A sample of filtered air was isolated in the counter, the air being then diverted through the counter bypass tube.

17.0 A measurement of nucleus concentration in the filtered air sample was made. This was always zero, showing that the air was being effectively filtered.

17.30 The air sample in the flask was isolated, by clamping shut the inlet and outlet tubes to the flask.

18.0 The irradiation of the air in the flask was commenced, by removing the shutter between the UV lamp and the flask, as usual.

24.0 The irradiation of the air in the flask was stopped, and the inlet and outlet tubes to the flask unclamped.

24.10 The airflow from the flask through the counter was commenced, by restarting the pump. The rate of airflow used was 3.0 litres per minute. The airflow was continued for 20 seconds only, so that a volume of about 1.0 litre of irradiated air was removed from the flask, and replaced by filtered air coming in at the bottom of the flask. The total volume of the flask was 6.5 litres, and it was later measured, by filling the flask with water, and measuring the volume of the water, using a graduated cylinder.

24.30 A sample of the irradiated air was now isolated in the nucleus counter. At the same time, the air sample in the flask, containing nuclei, was again isolated, by clamping shut the inlet and the outlet tubes. The air sample in the flask was now left isolated for a time t seconds, to allow the concentration of nuclei to fall, through coagulation.

T (mins. and secs.)

25.30 A measurement of the nucleus concentration Z_o', in the air sample in the counter was made. It was assumed that Z_o' was also the concentration of nuclei in the 5.5 litres of irradiated air left in the flask, and mixed with 1.0 litre of filtered, nucleus free air, at T = 24.30. It was also assumed that these nuclei were mixed throughout the whole volume (6.5 litres) of the flask, shortly after isolating the air in the flask for the coagulation period. Therefore Z_o, the concentration of nuclei in the air in the flask, at the commencement of the coagulation period, at T = 24 mins. 30 sec. was assumed to be given by

$$Z_o = \frac{Z_o' \cdot 5.5}{6.5} \qquad (24)$$

t + 24.10 The inlet and outlet tubes to the flask were unclamped, and the airflow through the flask was commenced again, at the rate of 3.0 litres per minute. The air from the flask was drawn through the counter, for 20 minutes, thus removing one litre of air from the flask.

t + 24.30 A sample of air from the flask, containing nuclei which had been allowed to coagulate for time t, was isolated in the nucleus counter, for a measurement of nucleus concentration.

t + 25.30 A measurement of nucleus concentration in this air sample was made. It was assumed to be the same as the nucleus concentration Z_t in the air in the flask, at time t + 24.30.

Calculation of radius of nuclei:

Measurements were available for Z_o the concentration of nuclei in the flask, at the commencement of the coagulation period; for Z_t the concentration at the end of the coagulation period, and for t, the duration of the coagulation period. A number of experiments were carried out, with different coagulation periods ranging from 2.0 minutes to 10.0 minutes. Table 6 shows corresponding values of Z_o, Z_t and t, from 9 different experiments.

It was assumed, in accordance with condition (14), that the loss in nucleus concentration, through mutual coagulation of the nuclei, was much greater than the loss from diffusion to the walls of the flask, and through sedimentation. Equation (23) was therefore applied, using the values of Z_o, Z_t and t, in Table 6, to calculate the value of r_o, the radius of the nuclei in each experiment, 30 seconds after the completion of the 6.0 minute static irradiation. Table 6 shows the calculated values of r_o, for each experiment, Values of r_o were found to range from 0.31×10^{-7} cm to 4.1×10^{-7} cm. The value in seven of the experiments ranged from 0.31×10^{-7} cm to 0.79×10^{-7} cm., whereas in the two remaining experiments, r_o was 1.5×10^{-7} cm and 4.1×10^{-7} cm. The values of Z_o in both these experiments were the highest recorded in the 9 experiments, being 147,000 per c.c. and 128,000 per c.c. respectively. It was possible that in the measurement of Z_o' in these two experiments, that some of the smallest nuclei present in the counter were not activated, with the result that Z_o was an underestimate.

TABLE 6

t secs.	Z_o nuclei/c.c.	Z_t nuclei/c.c.	r_o 10^{-7} cm.
120	128,000	115,000	4.1
135	97,300	57,800	0.54
180	86,700	55,200	0.79
240	105,000	50,800	0.64
300	86 ,700	30,800	0.36
360	104,000	38,900	0.58
420	147,000	70,200	1.5
480	79,900	24,100	0.41
600	113,000	19,800	0.31

These small nuclei, would be able to grow to detectable size by coagulation, during the coagulation period t, so that they would be detected when Z_t was being measured. The result would be that the measured loss of nuclei during the time t would be an underestimate, so that r_o would be an overestimate.

Since the results of these experiments were not very satisfactory, it was felt that perhaps condition (14), which assumed that the loss of nuclei by diffusion to the walls of the flask, and by sedimentation was negligible, compared to loss by mutual coagulation, was not fulfilled. The applicability of this condition $\gamma Z^2 >> \lambda Z$ was therefore investigated. It was found that Nolan and Kuffel[60] quoted a value of 17×10^3 for the ratio of λ to γ for the vessel they had used, for nuclei less than 1×10^{-6} cm in radius. These authors had found that the ratio λ/γ was constant for a given vessel, for nuclei less than 1×10^{-6} cm in radius. It is assumed that the UV nuclei in the author's experiments were less than 1×10^{-6} cm in radius. γ does not vary with the dimensions of the vessel, but λ does, since λ_d is proportional to A/V, which is the ratio of the surface area to the volume of the vessel. The part of λ due to sedimentation under gravity, λ_g is neglected, since for nuclei of radius less than 1×10^{-6}, the velocity of fall, under gravity, c, is very small. The value of A/V for the vessel used by Nolan and Kuffel, was 0.084 cm^{-1}. The value of A/V for the flask used in the author's experiments was approximately 0.3, greater by a factor of 3.4 than Nolan and Kuffel's figure. This means that the value of λ/γ in the author's experiments was approximately 3.4 times the value of

λ/γ found by those authors, so that λ/γ for the flask, for nuclei less than 1×10^{-6} cm in radius, was approximately 58,000. Therefore for a concentration of nuclei of $Z = 116{,}000$ per c.c. the ratio of $\gamma Z^2/\lambda Z$ is 2, so that with the vessel used in the author's experiments the rate of fall of nucleus concentration, by mutual coagulation, was approximately twice the rate of fall of nucleus concentration through diffusion of nuclei to the walls of the flask, when the concentration of nuclei was 116,000 per c.c. The initial nucleus concentrations in the author's experiments, ranged from 79,900 to 147,000. Therefore it seems that losses of nuclei by diffusion to the walls of the flask were not negligible, and the fact that it was not taken into account, probably explains the unsatisfactory results obtained.

Therefore, it seems that the method used by the author was not a good method to use with such a small vessel as the borosilicate flask. However, it might be possible to use a similar method, successfully, with a much bigger vessel, so that diffusion losses would be negligible.

It seems therefore that the values of r_o obtained with the higher initial concentrations are the more reliable ones. It would seem therefore that the radii of the UV nuclei produced in the six minute static irradiations, were in the range 0.5×10^{-7} cm to 5×10^{-7} cm.

Other Workers' Results:

Mulcahy and Kuffel[29] found that the radii of UV nuclei produced in moist air, varied from 3×10^{-7} cm to 11×10^{-7} cm.

However the nuclei had grown by coagulation, for some time before measurement, so that they must have been initially smaller. Atkinson[20] found that the nuclei produced in a cloud chamber, by UV radiation, had diffusion coefficients at least as great as for (small) ions, which suggests that they have radii less than 1×10^{-7} cm. initially.

MEASUREMENT OF THE CRITICAL OVERPRESSURE FOR CONDENSATION ON UV NUCLEI IN THE COUNTER.

It was decided to try to get an approximate measurement of the sizes of the UV nuclei, by measuring the critical pressure expansion ratio for condensation on the nuclei in the Nolan-Pollak counter.

Theory:

The pressure expansion ratio, for the nucleus counter, is the ratio of the atmospheric pressure plus the overpressure (P_1), to the atmospheric pressure (P_2). The adiabatic expansion in the counter is made from the higher pressure P_1 to the lower pressure P_2. The corresponding volume expansion ratio (V_2/V_1) in the counter is given by the equation

$$P_1/P_2 = (V_2/V_1)^{1.4} \qquad (1)$$

since the expansion is adiabatic. The fall in temperature in the adiabatic expansion is given by the equation

$$T_1/T_2 = (V_2/V_1)^{0.4} \qquad (2)$$

where T_1 is the initial temperature, and T_2 is the lowest

temperature achieved in the expansion.

The supersaturation S, achieved in an expansion in the counter, is found from the equation

$$S = \frac{p_1}{p_2} \left(\frac{V_1}{V_2}\right)^{1.4} \qquad (3)$$

where p_1 and p_2 are the saturation water vapour pressures at the temperatures T_1 and T_2 respectively. It follows that if the critical overpressure needed in the counter in order to condense on particular nuclei is known, the corresponding critical supersaturation ratio S, can be evaluated, using equations (1), (2) and (3). Once the critical supersaturation for condensation on the nuclei is known, their radii can be calculated using the equation given on page (1),

$$S = \mathrm{Exp}(2\gamma M/\rho R T_2 r) \qquad (4)$$

assuming that the nuclei are either water droplets, or are wettable but not water soluble. γ is the surface tension, M the molecular weight, ρ the density of water. R is the universal gas constant, r the radius of the nucleus. Even if the nuclei are not water, or insoluble and wettable, this method gives a fair indication of the radii of the nuclei.

Experimental Procedure:

The static method of irradiation was employed, using outdoor air filtered through cotton wool. A very short irradiation time of 2.0 minutes was used, since it was desired to measure the critical overpressure for condensation on the nuclei, as soon as

possible after their formation. Several 2.0 minute irradiations were carried out, over a period of two days. The percentage extinction of the light beam in the counter was measured, on making an expansion of a sample of the irradiated air, with various overpressures. The overpressures used ranged from 20 mm. Hg. to 300 mm. Hg. In order to compensate for any change in nucleus production, over the period during which experiments were carried out, the overpressures were not used in ascending or descending order, from one experiment to the next, but were used in the order 300 mm, 20 mm, 290 mm, 30 mm, 280 mm ... and so on.

Fig. 16 shows a plot of the percentage extinction against the overpressure. It can be seen that the part of this curve corresponding to the overpressures 60 mm, to 90 mm, forms a straight line, cutting the overpressure axis at 58 mm. overpressure. This overpressure was taken to be the critical overpressure for condensation on the nuclei. The corresponding critical pressure expansion ratio is 1.076. From equation (1) the corresponding critical volume expansion ratio is 1.054. T_1, the initial temperature was 17°C, room temperature, and the final temperature T_2 was calculated to be 11°C. The critical supersaturation, calculated from equation (3) was 1.372. Equation (4) then gave a value of $r = 3.6 \times 10^{-7}$ cm, for the water droplet requiring the same critical supersaturation for condensation, as the nuclei.

It seems therefore that the UV nuclei are extremely small. The critical supersaturation method carried out gives an equivalent water-droplet radius for the largest nuclei, not for the average nuclei. If the material of the nuclei is hygroscopic, then their

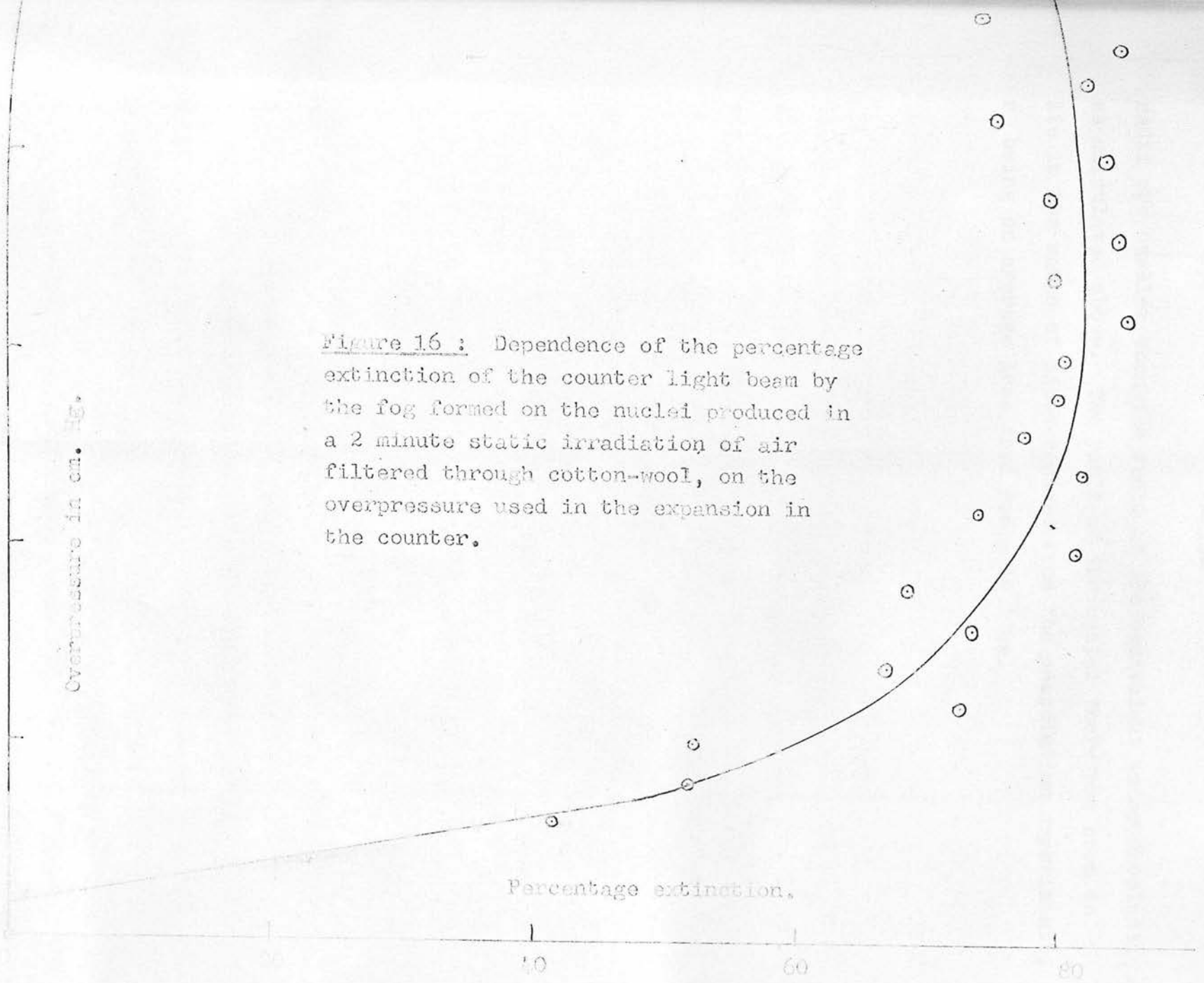


Figure 16 : Dependence of the percentage extinction of the counter light beam by the fog formed on the nuclei produced in a 2 minute static irradiation of air filtered through cotton-wool, on the overpressure used in the expansion in the counter.

radii are smaller than the radii of the equivalent water droplets, as calculated above. The radii of the nuclei therefore seem to lie in the range of sizes deduced from the coagulation experiments, r being on average less than 3.6×10^{-7} cm.

AN EXPERIMENT INVESTIGATING WHETHER UV NUCLEI ARE ELECTRICALLY CHARGED.

The following experiment was carried out, in order to find out whether the UV nuclei produced in the air in the flask, carried an electric charge, shortly after production. The method used depends on the principle that if the air containing the nuclei is passed through a cylindrical condenser, with a sufficiently high potential difference between the electrodes, then all the nuclei carrying electrical charges are removed from the air by being deposited on the walls of the condenser, under the influence of the electric field.

Theory:

The critical voltage V, required across the electrodes of a cylindrical condenser, in order to remove all ions of mobility W cm/sec. per volt/cm., with an airflow rate of Q cm^3/sec. through the condenser, is given by O'Connor and Flanagan(67), as

$$WV/Q = 1/4\pi C \qquad (1)$$

where C is the capacity of the cylindrical condenser. The relationship between the mobility of the charged nuclei, and their diffusion coefficients, may be obtained from the equation

$$D = 300\ kT\ W/q \qquad (2)$$

where k is Boltzmann's constant, T is the absolute temperature, and q is the charge on the nucleus, in electrostatic units. For a nucleus carrying a single electronic charge, at a temperature of

$15^{\circ}C$, equation (2) becomes

$$W = 40.3\ D \qquad (3)$$

It follows, that if one knows the diffusion coefficients of the largest nuclei, that a saturation voltage V which will remove all charged nuclei, can be calculated from equations (1) and (3). The largest nuclei, of course, have the lowest mobilities and thus need a greater potential difference across the condenser electrodes, to remove them from the air, than smaller nuclei do.

The cylindrical condenser:

Fig. 17 shows a diagram of the cylindrical condenser used. It consists of two brass cylindrical tubes mounted coaxially, the inner one streamlined and closed at the ends, and mounted between two discs of insulating material. These discs have large holes in them, symmetrically placed, in order to allow the airflow through the condenser. The air enters the condenser through either end tube, and passes through the narrow space between the cylinders. An electric field is obtained between the two cylinders by connecting the terminals, in contact with each, to a source of high tension.

Capacity of the condenser:

The capacity C of a coaxial cylindrical condenser, with air as the separating medium, is given by

$$C = \frac{0.2416\ k\ \ell}{\log_{10} a/b} \qquad (4)$$

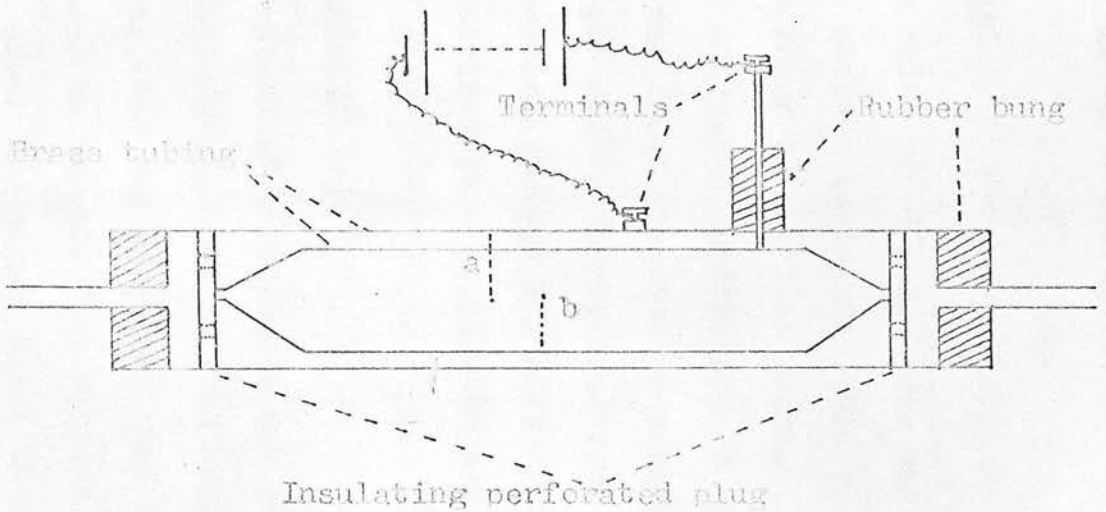


Figure 17 : Diagram of the cylindrical condenser used in the experiment investigating whether UV nuclei are electrically charged.

where k is the dielectric constant of air, assumed to be unity here, ℓ the length of the coaxial cylinders, a the internal radius of the outer cylinder, and b the external radius of the inner cylinder. The cylindrical condenser used by the author had the values a = 2.40 cm., b = 2.05 cm., ℓ = 65 cm., C was calculated to be approximately 230 cm.

Saturation Voltage:

An arbitrary value of 3×10^{-5} cm. was chosen for the radius r of the largest nucleus expected. This is much greater than the approximate value found in the last section, which was of the order 5×10^{-7} cm. The diffusion coefficient D corresponding to $r = 3 \times 10^{-5}$ cm. was found from tables prepared by Nolan[68], to be 0.493×10^{-6} cm^2 sec^{-1}. Using equations (1) and (3) the value of the saturation voltage was calculated to be approximately 290 volts for an airflow rate of 1 litre per minute.

Experimental Procedure:

The dynamic method of irradiation was employed, using an airflow rate of 1 litre per minute. The usual arrangement of apparatus was used, with the exception that the cylindrical condenser was placed in the air line between the flask and the nucleus counter. After the steady state nucleus concentration had been reached, three measurements of nucleus concentration were made, at intervals of 3.0 minutes, with no voltage across the electrodes of the condenser. The voltage across the condenser was now switched to 1 KV, much higher than the saturation voltage,

and three more measurements of nucleus concentration made. Finally, the voltage was switched to zero again, and three more measurements of nucleus concentration made. Ample time was allowed, after changing the voltage across the condenser, for the condenser and the counter to be filled with a completely new sample of irradiated air. The mean concentration of nuclei with the voltage switched off was 23,800 per c.c., and the mean concentration with the voltage at 1 KV, was 28,500. Within the limits of experimental error it seemed therefore that few, if any, nuclei were removed by the electric field in the condenser. It was therefore assumed that the UV nuclei were largely and probably completely uncharged, shortly after production. Most of the nuclei and probably all of them must have been uncharged on production, as they would not lose their charges in the short time between being produced, and entering the condenser.

Agreement with other workers' results:

Mulcahy and Kuffel[29] found that 5°/o to 18°/o of the nuclei produced in humid air or humid argon were electrically charged. However, they had usually allowed their nuclei to stand for five minutes in the irradiation chamber before sampling them, and some of the nuclei probably obtained electrical charges from small ions produced in the chamber by natural ionizing radiation.

Atkinson[20] found that the UV nuclei produced by UV radiation in a conventional cloud chamber containing air and water vapour were completely uncharged electrically.

Conclusion:

It seems therefore that the UV nuclei are not formed as a result of any ionization of the molecules of gases or vapours in the air, by the UV radiation. The energy of the photons of the UV radiation used in the author's experiments, with $\lambda > 2900A$, is not sufficient to ionize molecules of any gases or vapours known to be present in atmospheric air. The wavelengths corresponding to the ionization potentials of O_2, N_2, CO_2 are 990A, 760A and 860A respectively. Wavelengths corresponding to the ionization potentials of other common atmospheric trace gases such as sulphur dioxide, nitrogen dioxide, ammonia, hydrogen sulphide, carbon monoxide and nitrous oxide, are all below 1350A. McHenry and Twomey[23] found that no ionization of moist air was produced by UV radiation containing wavelengths down to 2300A, at least.

On the other hand, Norinder and Siksna[69,70], and Vassails[27] found that large ions appeared in air after UV irradiation However Norinder and Siksna, decided that these large ions were produced when electrically neutral condensation nuclei already formed in the gas, captured electrons which were emitted from solid bodies due to a photoelectric effect caused by the UV radiation. They proposed that the nuclei were formed in the air by some chemical process, due to the UV light.

ATTEMPTED SELECTIVE REMOVAL OF CERTAIN TRACE GASES OR VAPOURS FROM ATMOSPHERIC AIR.

It was thought that if certain trace gases could be selectively removed from the atmospheric air before irradiation, then the UV nucleus production in the remaining air would indicate which trace gases were responsible for nucleus formation. Thus if trace gas or vapour X (assumed to be responsible for UV nucleus formation), were removed, no UV nuclei should be produced on UV irradiation of the remaining air. However it proved impossible to remove trace gases such as sulphur dioxide, specifically. Whichever method was thought of, it always involved passing the atmospheric air through some reagent, either in liquid form, or impregnated on a filter paper. Invariably the reagent removed many other trace gases as well as the specified one, and often the reagent contaminated the air passing through it. For example, when the atmospheric air was drawn in to the flask through a filter paper impregnated with ammoniacal zinc nitroprusside, which removes sulphur dioxide from the air, some free ammonia was added to the air, and this caused copious nucleus formation in the air, on irradiation. The result of using the above general method, was therefore not very informative, and its use was discontinued.

POSSIBILITY OF VARYING THE RELATIVE HUMIDITY OF THE ATMOSPHERIC AIR, BEFORE IRRADIATION:

The usual method employed for varying the relative humidity of air is the split-stream method, in which some of the air is passed through a humidifier, and the rest of it through a drying tube containing some drying agent such as silica gel. Various relative humidities, ranging from a few per cent to saturation, are achieved by varying the proportion of the air passing through each device. However, passing the air through the humidifier invariably removes a fraction, if not all, of water soluble trace gases and vapours, whereas most drying agents such as silica gel, also remove certain trace gases and vapours. A freeze-trap used to dry the air, partially removes certain trace gases and vapours.

For these reasons, an experiment in which the relative humidity of the air to be irradiated, was varied, was not attempted.

DEPENDENCE OF STEADY STATE UV NUCLEUS FORMATION IN FILTERED OUTDOOR AIR ON ATMOSPHERIC SULPHUR DIOXIDE CONCENTRATION AND ON VARIOUS METEOROLOGICAL MEASUREMENTS.

It was thought that it would be interesting to compare the UV nucleus formation in UV irradiated, filtered air, with the sulphur dioxide concentration in the air, and with current meteorological conditions. Many workers have suspected that sulphur dioxide plays a part in the formation of nuclei, by UV radiation, in atmospheric air. If this supposition was true, it was expected that UV nucleus formation in the filtered air, would show a similar variation, to the sulphur dioxide concentration in the air, from experiment to experiment.

Method for the measurement of sulphur dioxide concentrations in air:

The method used for the measurement of the sulphur dioxide concentration in atmospheric air, was a modification of the ammoniacal zinc nitroprusside test paper method recommended by "Sulphur Dioxide", Booklet No. (3), Methods for the detection of toxic substances in air, H.M. Factory Inspectorate[71]. An ammoniacal zinc nitroprusside test paper, was mounted in a Millipore filter holder. The air to be tested, was drawn through the filter paper, at a recommended rate of airflow, per unit area of paper penetrated by the airflow. Sulphur dioxide in the air under test causes the surface of the exposed area of the test paper to turn a brick-red colour. The amount of brick-red colour developed, depends on the sulphur dioxide concentration in the

air, and on the volume of air passed through unit area of the test paper. In the author's experiments, the area of paper penetrated by the air under test, was circular, 2 cm. in diameter. With the sulphur dioxide concentrations obtained, which ranged from 1.4 pphm (part per hundred million parts of air) to 30 pphm, it was found that a sampling period of 2 hours, 24 minutes, using an airflow rate of 1.6 litre per minute, gave best results. When the airflow rate was faster than this, some of the red colour was developed on both sides of the paper, showing that all the sulphur dioxide in the air, was not being absorbed in the test paper. When the airflow rate was slower than 1.6 litres per minute, the red colour did not develop rapidly enough to give a measurable colour content after the above sampling period. The colour density of the test paper surface, after the test, was measured by using a reflectometer. A reflectometer measures the fraction of light reflected from the surface of the test paper, onto a photocell, the photocell current being measured by a sensitive microammeter. Five standard colour stains, with different colour densities corresponding to certain concentrations of sulphur dioxide, for a particular volume of air sampled, are supplied with the Factory Inspectorate booklet[71]. The stain obtained on the test paper was compared with the standard stains, by using the reflectometer. Reflectometer readings were taken for the standard stains which were immediately darker and lighter than the test stain, and for the test stain itself. By suitable interpolation, the sulphur dioxide concentration in air, corresponding to the test stain, was obtained. The colour density of the test paper was always measured immediately after the air sampling period, as the colour

deteriorated if the test paper were stored for even a few hours.

Preparation of the Test Papers:

50 c.c. of a 6% W/V solution of zinc sulphate heptahydrate, in deionized water, were added with stirring to 50 c.c. of a 10% W/V solution of sodium nitroprusside in deionized water. Solid ammonium acetate was added gradually, with stirring, to the mixture, until the precipitated zinc nitroprusside had dissolved. Finally, 20 c.c. of glycerol were added, and the solution was stirred again. 47 mm. circles of Whatman's No. 1. filter paper were thoroughly soaked in the solution. The superfluous liquid was allowed to drain off, and the papers were dried for 40 minutes in a well ventilated oven, at a temperature of 30°C. The test papers were stored in an airtight glass container, in the dark. Fresh test papers were prepared every ten days, although according to the instructions booklet, they are stable for about one month.

Choice of Method:

This method for the measurement of sulphur dioxide concentration in air, was chosen, because it is a relatively simple method to use, not requiring elaborate chemical laboratory equipment. This method is also a specific method for determination of sulphur dioxide. Hydrogen chloride, at a concentration of 15 ppm gives only a very faint stain, and carbon disulphide, at concentrations of up to at least 500 ppm, yields no stain, according to the booklet(71).

Preliminary Experiments:

The first experimental procedure used, in order to find out if there was a relationship between the UV nucleus production in filtered air, and the sulphur dioxide concentration of the air was as follows: The sulphur dioxide concentration in the atmospheric air was measured, for a standard sampling period. At the beginning, and end of this sampling period, the concentrations of UV nuclei produced in three 6.0 minute static irradiations, of the outdoor air, filtered through cotton wool, were measured. Care was taken that experimental conditions, such as the time of flushing of the flask with the filtered air, were similar for each measurement.

After twelve different experiments, carried out on different days, the mean values of each six measurements of UV nucleus concentration, were compared with the corresponding sulphur dioxide concentrations, in order to find out if there was a significant correlation. The U-V nucleus concentrations ranged from 41,300 per c.c. to 225,000 per c.c., and the sulphur dioxide concentrations ranged from 2.5 pphm to 30 pphm. The rank order correlation coefficient, applied to corresponding measurements, had a value of -0.04, indicating no correlation. The rank order correlation coefficient ρ, for two sets of corresponding data, is defined as

$$\rho = 1 - \frac{6\Sigma d^2}{N(N^2-1)} \qquad (1)$$

where N is the total number of cases, and d is the difference between the rank number of corresponding data, each arranged in order.

It seemed therefore as if there was no significant correlation between the UV nucleus production in filtered atmospheric air, and the sulphur dioxide concentration of the air.

Effect of cotton wool filter:

It was during the course of some exploratory experiments, carried out at this stage of the work, that it was discovered that the cotton wool filter was affecting the UV nucleus forming capacity of the air filtered through it. As is discussed in more detail on page 32 it was proposed, with good evidence, that the cotton wool filter, was in fact "damping out" natural fluctuations in the concentration of the trace gas X responsible for UV nucleus formation. In other words, it was thought that during experiments when the concentration of X in the air was higher than average, that the cotton wool absorbed some of X, thus reducing the concentration. On the other hand, it was thought that if the concentration of X in the outdoor air were lower than average, that the cotton wool would desorb some of X, absorbed during previous experiments, into the air, thus increasing the concentration.

It was therefore decided to use Millipore filters in any future experiments, investigating the correlation between the production of UV nuclei in filtered air, and the sulphur dioxide concentration in that air. It was also decided to use the dynamic

method of irradiation, for nucleus production, and to compare the steady state nucleus concentration, under standard conditions, with the sulphur dioxide concentration in the air before irradiation. The detailed experimental procedure will now be described.

Arrangement of Apparatus:

This final arrangement of apparatus and experimental procedure was decided upon after a number of exploratory experiments. Fig. 18 shows the normal arrangement of apparatus, in schematic form. The outdoor air to be tested for UV nucleus formation, was drawn in through a wide-bore tube passing through a hole in the frame of a closed window of the room. The hole was about twelve feet above ground level outside the window. The air was then filtered through a 1.2 micron pore size Millipore filter, in a stainless steel holder, and drawn through the borosilicate flask, at a flow rate of 1 litre per minute. The air entered the flask through a long borosilicate glass tube, with its opening at the bottom of the flask, inside, and it left the flask through either the Nolan-Pollak counter bypass tube (normally), or through a tube leading to the counter. Both these tubes were connected to the flask at the top, so as to ensure maximum ventilation of the flask, by the air passing through it. By adjusting a three way tap, the air from the flask could be drawn through either the Nolan-Pollak counter, or its bypass tube. The tubing which carried the air from the flask to the counter was of wide bore (internal diameter = 1.2 cm.), and was a minimal length of 30 cm., in order to reduce losses of nuclei by diffusion to the walls of the tubing. The rate of airflow through the flask

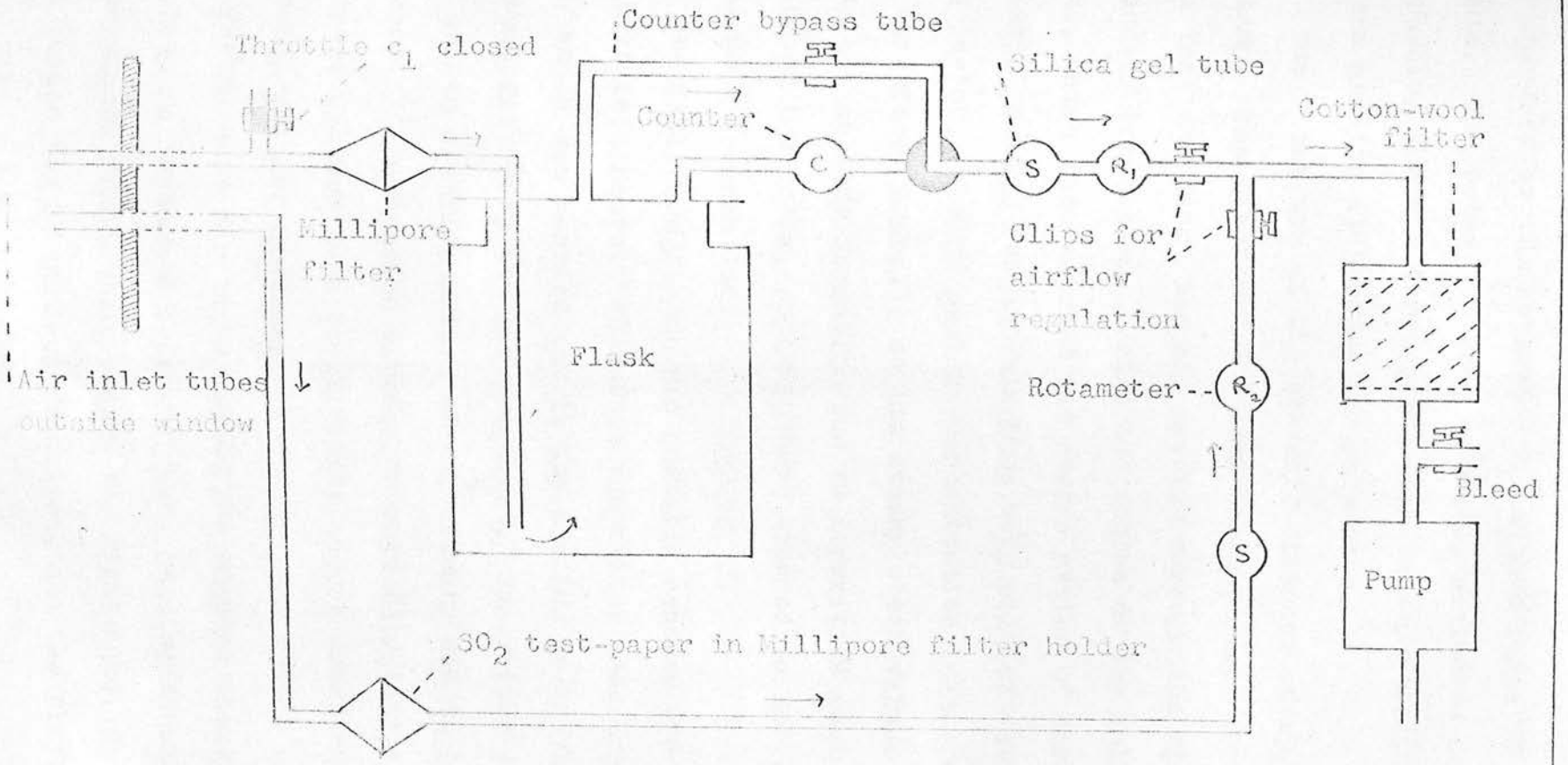


Figure 18 : The arrangement of apparatus used in the experiments investigating dependence of UV nucleus production on the sulphur dioxide concentration in the air. Arrows show direction of airflow.

was measured by the rotameter R_1, with a range of 0-1 litre per minute. The rotameter was, as usual, protected from condensation by passing the air through a drying tube containing silica gel, before passing it through the rotameter.

The flask was at the standard distance of 15.7 cm. from the UV lamp. The flask and the lamp were kept cool during irradiation by a ten inch fan. The air passing through the flask was continuously irradiated, during the course of the following experiments, which were carried out over a period of three months. The UV lamp, cooling fan and air pump were all left switched on during this period. The UV nucleus concentration in the air in the flask, was therefore generally at its steady state value. Any possible transient nucleus formation due to impurities occluded on the inside of the flask, ought to have decayed to zero, due to this continuous irradiation.

The Millipore filter was normally renewed every day, always at about 18.0 hours. Therefore the filter used during an experiment, which was carried out in the morning or in the afternoon, had been filtering the air overnight. The filter was used for this length of time, before an experiment, due to the observation by Junge[51], mentioned already on page 83 , that newly used Millipore filters seem to partially absorb some trace gases, including sulphur dioxide.

The outdoor air to be tested for sulphur dioxide concentration, was drawn in through a separate tube, passing through a second hole in the window frame, just beside the first tube, so that the air to be tested for UV nucleus formation, and the air to be tested

for sulphur dioxide concentration, both came from the same location. The air to be tested for sulphur dioxide concentration, was drawn at the standard rate of 1.6 litre per minute through an ammoniacal zinc nitroprusside test paper, which was mounted in an aluminium filter holder. The airflow for this sulphur dioxide test, which was only carried out during each experiment, was provided, as can be observed in Fig. 18, by the same vacuum pump that provided the flow of filtered air through the flask. The rate of airflow through the test paper was measured by a rotameter R_2 with the range of 0.5 - 5.0 litres per minute. The lengths of rubber tubing from the air inlets outside the window, to the flask and to the sulphur dioxide test paper, were exactly the same, so that any loss of sulphur dioxide, by absorption on the tube wall, ought to be nearly the same in each tube. The sulphur dioxide concentration in the air passing through the flask, ought to be very nearly the same as the sulphur dioxide concentration in the air passing through the sulphur dioxide test paper.

Measurement of outdoor nucleus concentration:

Fig. 19 shows, in schematic form, the modification made to the arrangement of apparatus when it was required to measure the concentration of condensation nuclei in outdoor air, during an experiment. The tube leading from the flask to the photo-electric counter was clamped shut, by closing the throttle c_2. Unfiltered outdoor air was drawn through the nucleus counter, through wide-bore rubber tubing, the throttle c_1, on this tubing, being now open. A second vacuum pump, was used for this purpose and the

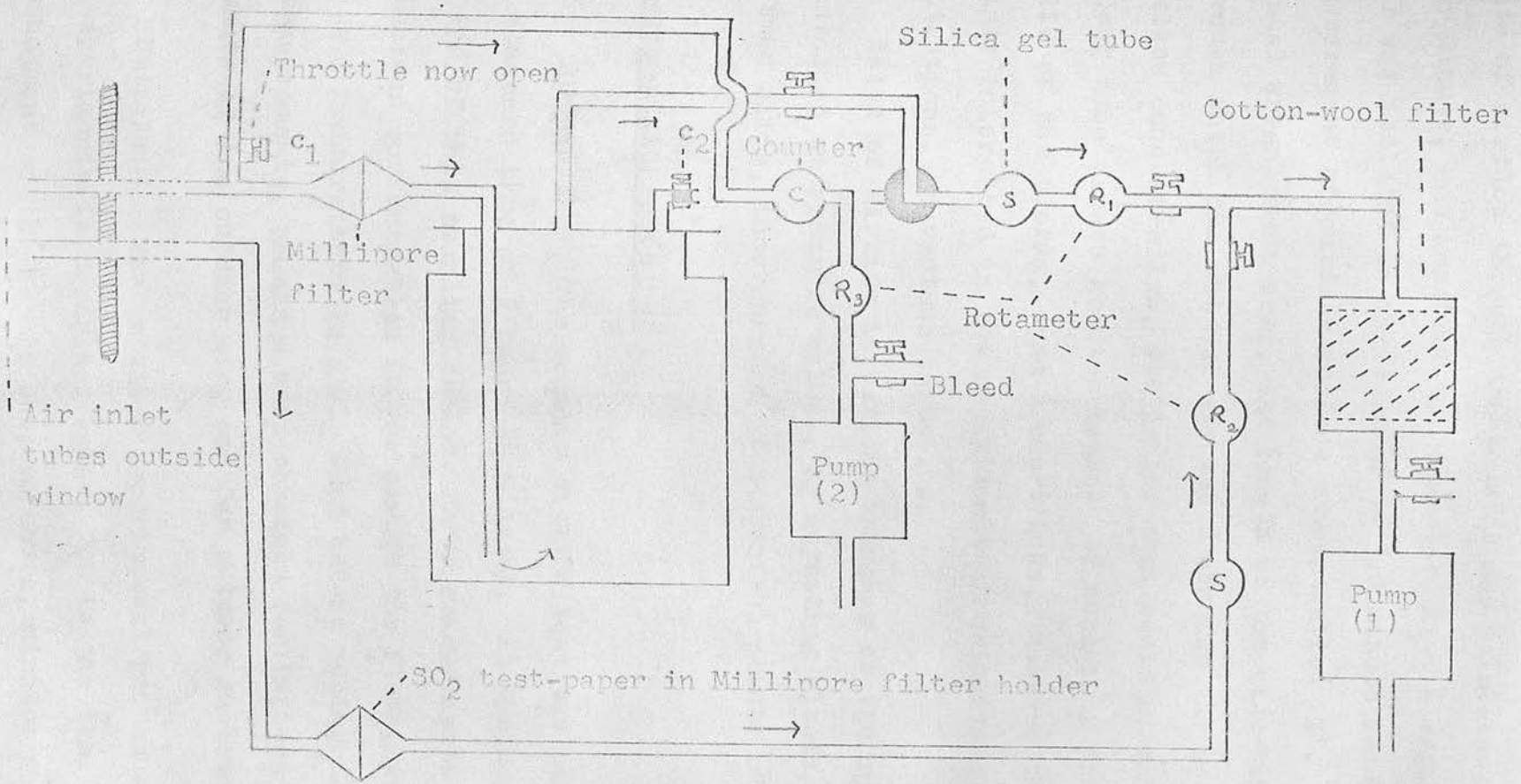


Figure 19 : The modified arrangement of apparatus used when measurements of the concentration of condensation nuclei in outdoor air were being made. The arrows show the direction of airflow.

rate of airflow through the counter was maintained at 4.0 litres per minute, and measured by rotameter R_3. A sample of outdoor air was isolated in the counter at 3.0 minute intervals, for measurement of outdoor nucleus concentration Z'. In the experimental arrangement used, the length of the wide-bore tubing through which the outdoor air was drawn for the measurement of nucleus concentration, was longer than would normally be used. A long tube causes greater losses of nuclei by diffusion to the walls of the tubing, than a short tube. However the author was mainly interested in the measurement of relative nucleus concentrations, on various occasions.

Rates of airflow in various branches of the apparatus, were maintained at specific values, by adjusting bleeds, throttles, and Hoffman clips, incorporated at convenient points of the apparatus.

Experimental Procedure:

(a) Summary: The sulphur dioxide test was carried out for the standard time of 2 hours 24 minutes. At the beginning, middle and end of this sampling period, three measurements of steady-state UV nucleus concentration in the air in the flask, were carried out, making 9 measurements in all. Just before making the middle set of measurements, readings were obtained for various meteorological elements of the outdoor air, and for outdoor nucleus concentration.

(b) Detail: The detailed experimental procedure used for all experiments is described below. T is the time after the commencement of the experiment, in hours, minutes and seconds.

T

0. 0. 0 The airflow through a newly mounted sulphur dioxide test paper was commenced, at the standard rate of 1.6 litre per minute. Since the air in the flask was continuously irradiated, UV nucleus concentration in the air was at the steady state value. At this time, the irradiated air was passing from the flask through the nucleus counter bypass tube.

0. 1. 0 The three-way tap was adjusted so that the irradiated air from the flask now passed through the nucleus counter.

0. 3. 0 A sample of irradiated air was now isolated in the counter, by adjusting the three-way tap, so that the air from the flask passed through the counter bypass tube again, and by closing the counter inlet and outlet taps. The first measurement of steady state UV nucleus concentration was made, at the standard overpressure of 160 mm. Hg.

0. 4. 5 The irradiated air from the flask was passed through the counter again.

0. 7. 0 The second measurement of UV nucleus concentration was now made, in the same way as the first one.

0.10. 0 The third measurement of UV nucleus concentration was made in the same way.

0.10. 5 The irradiated air flow was switched over from the bypass tube to the counter, to clear up the fog formed in the counter.

0.11. 0 The flow or irradiated air was switched back to the counter bypass tube.

T

0.55. 0 Various Meteorological elements of the outdoor air were measured, using instruments mounted on the roof of the Department of Natural Philosophy, and owned by the Department of Meteorology, University of Edinburgh. The meteorological elements measured were: dry bulb temperature, wet bulb temperature, minimum temperature, and maximum temperature, all in a Stevenson screen; wind direction was found, approximately, by observing a wind vane; wind speed, averaged over a period of ten minutes, was measured by means of a recording anemometer. The temperature of the room in which the experiment was carried out, was also measured.

1. 6. 0 The flow of irradiated air from the flask was switched from the counter bypass tube, to the counter.

1. 8. 0 A sample of irradiated air was isolated in the counter.

1. 9. 0 The fourth measurement of the steady state UV nucleus concentration, Z made.

1.12. 0 The fifth measurement of Z was made.

1.15. 0 The sixth measurement of Z was made.

1.15. 5 The apparatus was quickly modified in accordance with Fig. 19, in order to measure the concentration of outdoor nuclei Z' .

1.19. 0 A sample of unfiltered outdoor air was isolated in the counter.

1.20. 0 The first measurement of Z' was made.

1.23. 0 " second " " " "

1.26. 0 " third " " " "

T

1.29. 0 The fourth measurement of Z' was made.

1.32. 0 " fifth " " " "

1.35. 0 " sixth " " " "

1.35. 5 The apparatus was restored to its normal arrangement, as in Fig. 18, with the irradiated air passing through the counter bypass tube.

2.11. 0 The flow of irradiated air from the flask was diverted through the counter again.

2.13. 0 A sample of irradiated air was isolated in the counter.

2.14. 0 The seventh measurement of Z the steady state UV nucleus concentration, was made.

2.17. 0 The eighth measurement of Z was made.

2.20. 0 The ninth measurement of Z was made.

2.20. 5 The airflow was switched back from the counter bypass tube to the counter, in order to clear away the fog formed in the counter.

2.21. 0 The airflow was diverted back to the bypass tube.

2.24. 0 The sampling of the air for sulphur dioxide was stopped. The sulphur dioxide concentration was immediately evaluated, by measuring the brick red colour density, of the exposed surface of the test-paper, using the reflectometer, as previously explained.

2.24. 0 The shutter was placed between the UV lamp and the flask, as it was wished to check that there were no nuclei present in the air in the flask, in the absence of UV irradiation.

3.10. 0 The airflow was diverted from the counter bypass tube, to the counter.

T

1.29. 0 The fourth measurement of Z' was made.

1.32. 0 " fifth " " " "

1.35. 0 " sixth " " " "

1.35. 5 The apparatus was restored to its normal arrangement, as in Fig. 18, with the irradiated air passing through the counter bypass tube.

2.11. 0 The flow of irradiated air from the flask was diverted through the counter again.

2.13. 0 A sample of irradiated air was isolated in the counter.

2.14. 0 The seventh measurement of Z the steady state UV nucleus concentration, was made.

2.17. 0 The eighth measurement of Z was made.

2.20. 0 The ninth measurement of Z was made.

2.20. 5 The airflow was switched back from the counter bypass tube to the counter, in order to clear away the fog formed in the counter.

2.21. 0 The airflow was diverted back to the bypass tube.

2.24. 0 The sampling of the air for sulphur dioxide was stopped. The sulphur dioxide concentration was immediately evaluated, by measuring the brick red colour density, of the exposed surface of the test-paper, using the reflectometer, as previously explained.

2.24. 0 The shutter was placed between the UV lamp and the flask, as it was wished to check that there were no nuclei present in the air in the flask, in the absence of UV irradiation.

3.10. 0 The airflow was diverted from the counter bypass tube, to the counter.

T

3.12. 0 A sample of air from the flask was isolated in the counter.

3.13. 0 A measurement of the nucleus concentration in the air from the flask, was made. The air was no longer irradiated, after T = 2.24. 0, so that any UV nuclei already present should have been swept out of the flask, by the filtered air. This measurement was invariably zero. It afforded a convenient way of checking on the efficiency of the filtering of the outdoor air by the Millipore filter. It also showed that there was no leak in the apparatus, which would allow room air containing nuclei into the apparatus. This measurement also made it clear, that no nuclei were produced in the flask, without UV irradiation, which would be detected in the nucleus counter, at the standard pressure expansion ratio of 1.21.

3.13. 5 The shutter between the UV lamp and the flask was removed again, and the flask and the air passing through it, were left exposed to the UV radiation, until the next experiment.

Time of experiments: The experiments were usually carried out during the afternoon, as an uninterrupted time of about four hours was required for each experiment. However a few experiments were carried out during the morning.

Results:

Table 7 shows the results of all 41 experiments, carried out over a period of nearly three months, between the 13th March 1967 and the 6th June 1967. The various items are numbered from (1) to (23). The numbers correspond to the following data:

(1) : the date on which the particular experiment was carried out.

(2) : The day of the week on which the experiment was carried out.

(3) : The time of day on which the experiment was commenced, that is when T = 0.0.0 in the experimental procedure.

(4) : This is Z_1, the mean of the first three measurements of steady state UV nucleus concentration in the irradiated air from the flask, expressed in nuclei per c.c. of air.

(5) : is Z_2, the mean of the second set of three measurements of steady state UV nucleus concentration in the irradiated air.

(6) : is Z_3, the mean of the third and last set of three measurements of steady-state UV nucleus concentration in the irradiated air.

(7) : Z is the mean of Z_1, Z_2 and Z_3.

(8) : This gives the deviation factor d of Z. It is defined as the difference between the largest of the three mean concentrations, Z_1, Z_2, Z_3, and the smallest of these three, divided by the mean of Z_1, Z_2, Z_3, which is Z.

$$d = \frac{\text{largest } Z - \text{smallest } Z}{\text{mean } Z} \qquad (2)$$

d is small, if the UV nucleus concentration remains fairly constant from the first set of measurements, to the third and last set. d is relatively large, when UV nucleus concentration varies a lot, over the 2 hour 24 minute duration of an experiment. d has a maximum value of

TABLE 7

		1967			
1.	Date: Day, Month	13 March	14 March	15 March	16 March
2.	Day of week	Monday	Tuesday	Wednesday	Thursday
3.	Time: hrs, mins.	14.30	9.38	14.33	-
4.	Z_1:nuclei/c.c.	1960	6110	2120	7570
5.	Z_2: " "	1200	4550	4,980	9520
6.	Z_3 " "	1510	4300	3220	11000
7.	Z " "	1560	4990	3440	9370
8.	Deviation: d	0.49	0.36	0.83	0.37
9.	Z':nuclei/c.c.	128,000	118,000	136,000	115,000
10.	U:SO_2 conc. (1) pphm	9.3	12.4	8.2	9.2
11.	SO_2 conc. (2) "	7.8	4.2	4.7	5.0
12.	Smoke O.D.	-	34.9	34.6	44.5
13.	Wind dir. (1) ^{o}	270	230	230	200
14.	Wind dir. (2) ^{o}	250	230	260	250
15.	Wind sp. (1) knots	11.5	15.0	11.5	5.5
16.	Wind sp. (2) "	11.8	22.8	21.2	13.1
17.	Wind sp. trend	N	N	N	N
18.	Rain (1) inches	0	0	0.14	0.03
19.	Rain (2) "	0	0	0.01	0
20.	Outdoor R.H. %	53	63	79	66
21.	Sunshine: hours	5.2	0.2	5.9	6.0
22.	Outdoor temp.: ^{o}F	46.0	51.0	39.1	48.9
23.	Room temp.: ^{o}F	62.6	61.5	-	64.6

TABLE 7 (Contd.)

1. 17 March	19 March	20 March	21 March	22 March	23 March
2. Friday	Sunday	Monday	Tuesday	Wednesday	Thursday
3. 14.42	15.44	14.26	9.43	14.21	14.58
4. 2,240	1	6,370	1,930	1,360	430
5. 2,490	2	7,240	2,190	3,490	77
6. 3,370	14	3,750	2,160	1,100	150
7. 2,700	6	5,780	2,100	1,980	219
8. 0.42	2.2	0.6	1.2	1.2	1.6
9. 141,000	43,000	127,000	110,000	111,000	134,000
10. 6.1	2.3	12.0	8.5	5.9	4.3
11. 4.2	1.4	3.8	4.7	5.7	4.5
12. 34.0	20.0	36.9	-	-	39.7
13. 250	250	250	230	230	270
14. 250	280	230	240	260	270
15. 18.0	20.0	14.5	14.0	-	16.7
16. 26.7	24.7	17.9	22.2	15.6	16.1
17. D	D	N	I	D	D
18. 0.06	0	0	0	0	0
19. 0	0	0	0	0	0
20. 64	49	79	62	74	48
21. 3.4	8.4	0.1	3.8	5.7	8.3
22. 45.3	50.5	51.0	51.0	46.1	45.6
23. 66.7	63.7	67.3	63.9	64.8	68.2

TABLE 7 (Contd.)

1.	24 March	25 March	27 March	30 March	1 April
2.	Friday	Saturday	Monday	Thursday	Saturday
3.	10.11	15.33	14.54	14.45	15.21
4.	198	18	130	4,550	263
5.	149	29	506	84	99
6.	64	97	1,550	56	24
7.	137	48	728	1,560	129
8.	0.98	1.7	2.0	2.9	1.9
9.	61,300	61,300	126,000	127,000	30,900
10.	4.5	3.1	5.8	3.3	2.7
11.	5.1	3.7	2.8	7.5	6.3
12.	-	-	-	44.9	-
13.	200	230	200	250	230
14.	230	230	240	300	200
15.	13.2	12.0	19.0	10.5	10.0
16.	16.2	17.2	17.5	6.9	12.6
17.	N	D	D	N	I
18.	0	0.04	0.07	0.01	-
19.	0	0	0	0	-
20.	78	81	65	34	67
21.	0.6	0.9	3.7	5.7	0.1
22.	44.2	48.8	44.9	48.2	41.7
23.	64.2	63.5	60.6	67.5	56.3

TABLE 7 (Contd.)

1.	2 April	3 April	4 April	5 April	21 April
2.	Sunday	Monday	Tuesday	Wednesday	Friday
3.	16.33	10.22	14.18	14.58	15.17
4.	1,240	9,650	40,000	335	557
5.	124	10,800	9,190	131	396
6.	801	9,480	5,230	94	157
7.	721	9,980	18,200	187	370
8.	1.5	0.13	1.9	1.3	1.1
9.	51,100	102,000	106,000	109,000	76,800
10.	4.9	14.3	6.6	2.8	2.2
11.	2.5	5.2	6.6	2.7	3.2
12.	26.8	42.4	35.9	26.6	-
13.	250	230	230	290	320
14.	250	250	250	310	310
15.	9.7	8.2	-	-	10.5
16.	14.2	14.2	21.4	21.8	11.0
17.	N	N	N	D	D
18.	-	-	0.003	0	0.01
19.	-	0	0	0	0
20.	76	70	65	43	35
21.	3.7	1.2	2.1	9.8	7.7
22.	44.5	46.6	52.0	47.5	47.1
23	61.5	61.9	65.5	-	67.6

TABLE 7 (Contd.)

1.	22 April	25 April	26 April	27 April	28 April
2.	Saturday	Tuesday	Wednesday	Thursday	Friday
3.	-	-	14.37	15.04	14.35
4.	251	9,720	376	328	7,810
5.	526	839	119	399	3,490
6.	453	700	347	-	1,120
7.	410	3,750	281	364	4,140
8.	0.67	2.4	0.91	-	1.6
9.	50,700	50,300	85,800	58,800	153,000
10.	3.8	5.0	3.0	2.3	3.2
11.	5.1	5.7	6.2	3.9	4.5
12.	36.8	-	-	-	36.6
13.	230	230	230	20	270
14.	-	-	220	250	260
15.	2.5	4.0	13.0	5.5	9.0
16.	5.2	5.7	8.7	5.3	11.4
17.	-	-	N	I	D
18.	0	0	0.001	0	0
19.	0	0	0	0	0
20.	54	50	55	43	53
21.	0.1	8.6	0.5	7.2	8.2
22.	42.6	54.8	51.6	60.0	68.8
23.	63.3	69.4	70.3	74.3	75.6

TABLE 7 (Contd.)

1.	29 April	5 May	6 May	9 May	10 May
2.	Saturday	Friday	Saturday	Tuesday	Wednesday
3.	14.27	14.34	15.02	14.25	14.48
4.	57	39	759	2,190	849
5.	73	143	649	814	1,420
6.	378	142	2,450	657	865
7.	169	108	1,290	1,220	1,040
8.	1.9	0.96	1.4	1.3	0.55
9.	57,900	43,000	68,200	83,500	81,400
10.	1.8	1.6	2.5	3.3	3.9
11.	3.7	7.1	5.2	5.5	5.1
12.	29.2	33.3	39.4	39.3	36.9
13.	250	70	90	230	230
14.	260	110	40	270	220
15.	9.5	11.0	6.0	-	2.0
16.	12.7	12.1	6.7	10.4	4.4
17.	N	N	D	N	D
18.	0	0.01	0.01	0	0.04
19.	0	0	0.01	0	0.02
20.	50	58	82	43	62
21.	10.3	1.8	0	10.7	1.3
22.	63.2	56.0	50.2	59.3	57.9
23.	73.0	73.4	70.0	71.8	72.1

TABLE 7 (Contd.)

1.	11 May	12 May	13 May	16 May	17 May
2.	Thursday	Friday	Saturday	Tuesday	Wednesday
3.	14.37	14.36	15.20	14.57	14.37
4.	2,230	758	107	11,500	3,440
5.	1,500	373	15	9,630	1,170
6.	18,300	356	105	7,480	2,270
7.	7,340	496	76	9,550	2,290
8.	2.3	0.81	1.2	0.42	0.99
9.	69,400	77,000	46,900	72,200	63,000
10.	5.2	3.3	1.4	5.8	5.8
11.	5.5	2.3	2.5	3.5	4.2
12.	47.8	35.8	32.2	-	37.7
13.	360	20	50	360	20
14.	50	70	90	60	70
15.	6.5	7.8	5.5	4.9	5.0
16.	5.8	7.5	6.4	5.5	6.7
17.	N	I	D	N	D
18.	0.01	0.57	0.05	0.50	0.17
19.	0.01	0	0.04	0.11	0.04
20.	96	84	87	93	89
21.	0	0	0	0	0.1
22.	47.7	49.2	45.7	44.0	43.5
23.	68.7	69.1	68.7	65.1	68.0

TABLE 7 (Contd.)

1.	19 May	22 May	30 May	1 June	2 June	6 June
2.	Friday	Monday	Tuesday	Thursday	Friday	Tuesday
3.	14.57	15.05	14.02	14.39	10.12	9.38
4.	5,110	13	1,460	4,910	1,910	4,690
5.	2,100	62	1,490	37	90,700	2,350
6.	845	25	185	438	208,000	3,560
7.	2,680	33	1,050	1,800	100,000	3,530
8.	1.6	1.5	1.3	2.7	2.1	0.66
9.	110,000	66,400	49,800	52,000	44,600	77,100
10.	4.8	2.4	2.7	2.2	4.6	5.9
11.	4.0	3.3	5.0	3.5	3.0	2.7
12.	-	-	29.4	39.2	33.5	-
13.	230	180	360	20	20	230
14.	260	120	50	-	-	-
15.	11.0	6.1	7.0	8.5	3.8	11.2
16.	14.0	10.0	5.6	-	-	-
17.	D	N	N	-	-	-
18.	0	0.04	0	0	0	0.02
19.	0	0	0	0	0	0.02
20.	46	56	79	77	72	82
21.	4.6	5.3	12.4	-	-	-
22.	57.5	54.0	56.4	55.0	56.1	52.1
23.	69.3	68.7	72.7	71.6	69.1	-

3.0. d therefore is a measure of the constancy of the steady state UV nucleus concentration, during an experiment.

(9) : The ninth line gives Z', which is the mean of the six measurements of outdoor nucleus concentration.

(10) : This is the average sulphur dioxide concentration, measured during the 2 hours 24 minutes duration of the experiment, and is expressed in pphm.

(11) : This is the average sulphur dioxide concentration for 24 hours, measured at Station (1), which lies in the centre of Edinburgh, about 0.5 mile north-north-west of the Department of Natural Philosophy, where the author's experiments were carried out. The map in Fig. 20 shows the locations of these two places. These measurements of sulphur dioxide concentration, were made as part of an air pollution survey carried out under the direction of Dr. Crosbie of the Geography Department, University of Edinburgh. The method used for the measurements, was the conductometric method. In the data kindly provided by Dr. Crosbie, the concentration of sulphur dioxide was expressed as micrograms of sulphur dioxide per meter cubed of air ($\mu g/m^3$). These figures were converted by the author to pphm, at a temperature of $10^{\circ}C$, so that they could be more easily compared with the author's own measurements, which are expressed in pphm. The conversion ratio used was

$$1 \text{ pphm } SO_2 \text{ at } 10^{\circ}C = 28.23 \ \mu g/m^3 \qquad (3)$$

(12) : The twelfth item is the "smoke" O.D. for 24 hrs., that is the optical density of the deposit of "smoke" or nuclei collected on the Millipore filter used to filter the outdoor air in the experiments, in that time. It is expressed as a percentage, and is defined here as $100(1 - B/W)$, where W is the reflectometer reading for light reflected from a control, white, Millipore filter which was unused, and B is the reflectometer reading for light reflected from the

Figure 1. Map of Edinburgh, showing location of Department of Natural Philosophy (*), Station 1 (1), and Station 2 (2). Arrow shows direction of nearby Turnhouse Airport.

deposit of "smoke" or nuclei on the used Millipore filter. The heavier the "smoke" deposit is, the higher the "smoke" O.D., and it is therefore an indication of the pollution of the outdoor air by "smoke" or condensation nuclei.

(13), (15), (20) and (23) give the values of the various Meteorological elements measured by the author on the roof of the Department of Natural Philosophy, approximately mid-way through the sulphur dioxide sampling period. These are

(13) : The wind direction at the time of observation. The direction is expressed in degrees of the compass, where 360° corresponds to a north wind, 90° to an east wind, 180° to a south wind and 270° to a west wind, and so on,

(15) : is the wind speed, in knots, averaged over ten minutes.

(20) : is the outdoor relative humidity , calculated from the wet bulb and dry bulb screen temperatures, using Meteorological Office tables.

(22) : is the outdoor dry bulb temperature in the Stevenson screen, in degrees Fahrenheit.

(23) : is the room temperature in degrees Fahrenheit,

(18) : This item is the rainfall for the last 24 hours, before the commencement of the experiment, expressed in inches. It was measured by means of a recording rainfall gauge, on the roof of the Department of Natural Philosophy.

(19) : is the rainfall for the last three hours before the commencement of an experiment, similarly measured. These figures are unfortunately, not very reliable, as the recording mechanism of the rainfall gauge did not keep very good time.

(14), (16), (17) and (21) are measurements obtained from the Meteorological Office, Edinburgh. They were taken at Turnhouse Airport, about 6 miles due west of the Department of Natural Philosophy. Facilities for similar measurements were not available at the Department of Natural Philosophy.

(14) : This is the average wind direction at Turnhouse, for the duration of each experiment.

(16) : This item gives the average wind velocity at Turnhouse, for the whole day.

(17) : The letters I, D and N are used to indicate the trend of wind velocity at Turnhouse, during the course of an experiment. I indicates that the wind velocity at Turnhouse was increasing. D indicates that it was decreasing, and N indicates that there was no marked trend to increase or decrease.

(21) : This gives the number of hours of sunshine, recorded at Turnhouse, for the day on which the experiment was carried out.

It is assumed that measurements (14), (16), (17) and (21) which were made at Turnhouse, are not very different from the values of these items, at the Department of Natural Philosophy, at the same time.

Discussion of Results:

It seems obvious, from corresponding measurements of Z, the mean steady state UV nucleus concentration (item (7)) in Table 7), and of U, the mean sulphur dioxide concentration, during an experiment (item (10)), that Z generally increased as U increased. Fig. 21 shows a plot of Z against U. Although there is some scatter, nevertheless Fig. 21 definitely shows that Z increases, generally, with U. If in Fig. 21, all the points with only one circle around them, are excluded, the relationship between Z and U becomes more noticeable, and the scatter of the points is much less. The excluded points are those points for which the value of Z, if in excess of 200 per c.c., has a deviation factor d (item 8

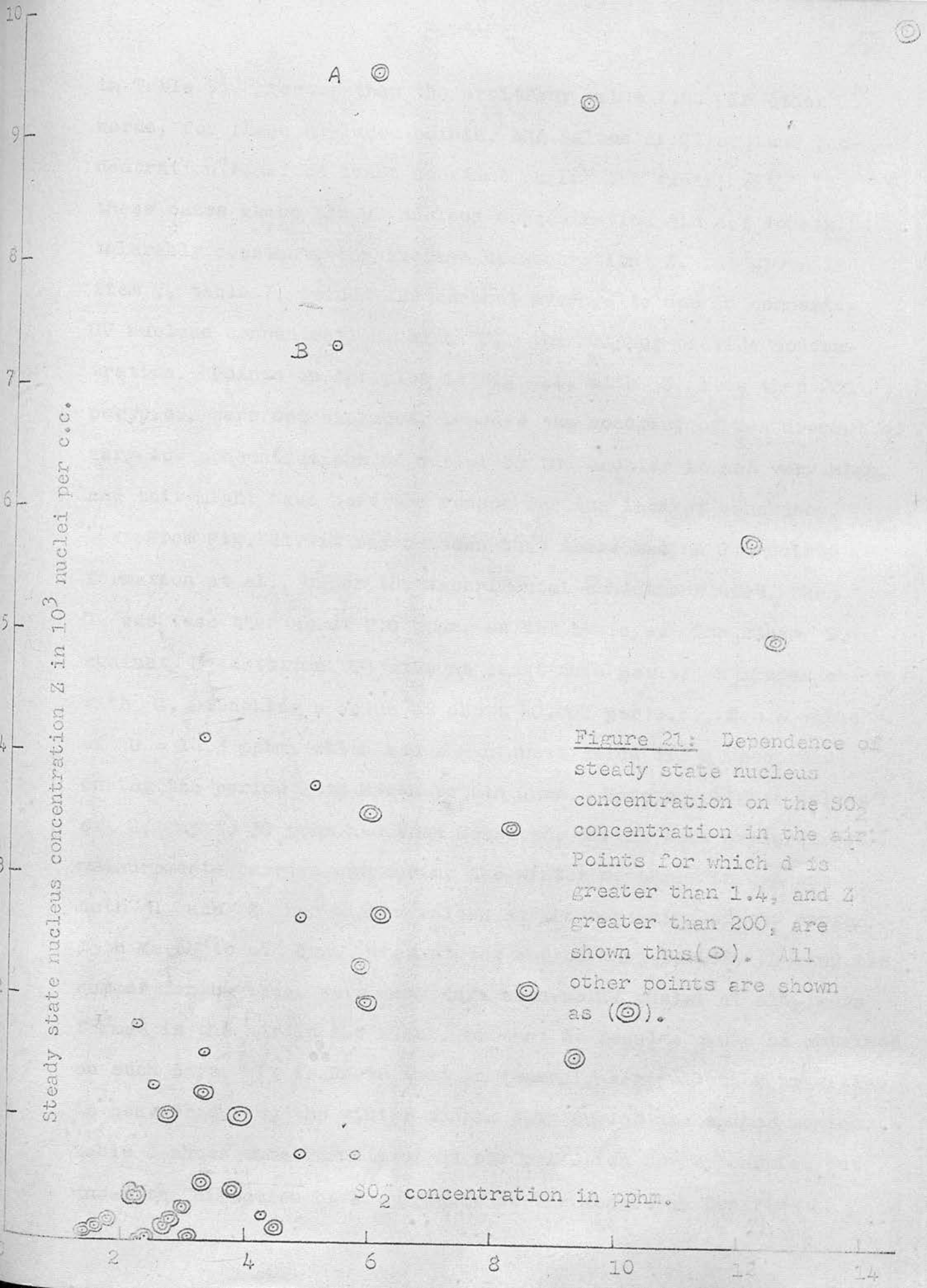


Figure 21: Dependence of steady state nucleus concentration on the SO_2 concentration in the air. Points for which d is greater than 1.4, and Z greater than 200, are shown thus(⊙). All other points are shown as (◎).

in Table 7), greater than the arbitrary value 1.4. In other words, for these excluded points, the values of UV nucleus concentration remained least constant during the experiment. In these cases where the UV nucleus concentration did not remain tolerably constant, the average concentration Z, as given in item 7, table 7, is not the correct average to use in comparing UV nucleus concentration, with U, the sulphur dioxide concentration. Points on the plot in Fig. 21, with Z less than 200 per c.c., were not excluded, because the accuracy of measurement of very low concentrations of nuclei by the counter is not very high, and this might have been the reason for the lack of constancy.

From Fig. 21, it may be seen that there was no UV nucleus formation at all, under the experimental conditions used, when U was less than about 2.0 pphm, on the average. The curve Z against U cuts the U axis at about this point. Z increases with U, reaching a value of about 10,000 per c.c., for a value of U = 14.3 pphm, which was the highest value of U recorded during the period 13th March to 6th June. However, higher values of U, up to 30 pphm had been measured, during some exploratory measurements carried out during the winter months. In general both U and Z had higher values at the beginning of the period 13th March to 6th June, than at the end of that period. During the summer months there were many days when no UV nuclei at all, were formed in the air in the flask, so that no results could be obtained on such days. It is known that in general, air pollution in cities is heavier during the winter months than during the summer months. Table 8 shows some results of an air pollution survey carried out under the direction of Dr. Crosbie of the Geography Department,

TABLE 8

Month	Average U' in pphm	Highest U' in pphm	Lowest U' in pphm	Days with U'>10 pphm	Days with U' < 2 pphm
		Station I			
Sept.'66	3.96	8.96	1.24	0	2
Oct. '66	6.65	10.9	3.44	2	0
Nov. '66	7.08	15.1	2.55	5	0
Dec. '66	6.94	17.8	1.31	2	1
Jan. '67	7.61	12.9	2.20	8	0
Feb. '67	6.69	11.9	3.01	4	0
March '67	3.96	7.79	1.38	0	3
Apr. '67	3.96	6.62	0.99	0	2
May '67	3.93	7.12	1.77	0	1
June '67	2.48	3.47	1.28	0	7
		Station 2			
Sept. '66	1.56	4.07	0.21	0	17
Oct. '66	2.52	4.74	0.96	0	11
Nov. '66	2.27	4.21	0.67	0	14
Dec. '66	1.42	2.87	0.50	0	17
Jan. '67	1.70	3.57	0.21	0	18
Feb. '67	1.31	2.98	0.21	0	21
March '67	0.64	2.94	0.0	0	23
Apr. '67	1.56	3.33	0.46	0	25
May '67	1.31	3.08	0.43	0	21
June '67	1.45	2.69	0.43	0	18

SO_2 Concentration 'U'', at Stations I and 2

All values of U' are averaged over 24 hours.

University of Edinburgh. Measurements of sulphur dioxide concentration U', were converted from $\mu g/m^3$ to pphm at $10^{o}C$ by the author. Table 8 gives the average value of U', the highest value of U', and the lowest value of U', measured for each month from September 1966 to June 1967, at Stations (1) and (2). Station (1), as has already been mentioned, lies in the centre of Edinburgh, one half mile north-north-west of the Department of Natural Philosophy. Station (2) lies in a southern suburban section of Edinburgh, not far from open country (see map in Fig. 20). The values of U' in table 8, are all average values for 24 hours. Since pollution is normally heavier during the day than during the night, due to the greater number of domestic fires, motor vehicles etc. in operation, it is to be expected that the sulphur dioxide concentration during the day, should be higher than U', the 24 hour average. Table 8 also shows the number of days in each month when U', the sulphur dioxide concentration was greater than 10 pphm at Station 1. January '67 had 8 days with U' greater than 10 pphm, whereas September, March, April, May and June had none. U' was never greater than 10 pphm at station 2. Also shown in table 8 are the number of days in each month, when U' was less than 2 pphm. It may be remembered that no UV nuclei were produced in the author's experiments when the sulphur dioxide concentration, was less than about 2 pphm. There were very few days when U' at station 1, was less than 2 pphm, especially in winter, whereas U' was generally less than 2 pphm at station 2.

It is certainly very clear from table 8, that the sulphur dioxide concentration in Edinburgh air is generally much higher in winter than in summer, especially in the centre of the city. This is probably due to the fact that more domestic fires are burning

during the winter months. Also, there is usually less mixing of the polluted air with clear air, during the winter months, in Edinburgh, so that heavy pollution of the air can build up.

Use of rank-order correlation coefficient:

The rank-order correlation coefficient ρ, already defined, was used in order to find out if there was any significant correlation between the measurements of Z, the mean UV nucleus concentration and the various other items for which corresponding measurements are given in Table 7. All values of Z were considered, when Z was less than 200 per c.c.; but only values of Z for which the deviation factor d was less than 1.4, were used, when Z was greater than 200 per c.c. The reasons for this selection of values of Z, were given earlier in this section. 29 values of Z fulfilled the above conditions.

Correlation of Z and U :

There was, as expected, a significant correlation ($\rho = 0.84$), between corresponding measurements of Z, the mean UV nucleus concentration, and U the sulphur dioxide concentration in the air, used in these experiments. This does not necessarily mean that the sulphur dioxide in the atmosphere was responsible for UV nucleus formation, as there may have been other trace gases and vapours whose concentrations in the air varied in a similar manner, to the sulphur dioxide concentration. However, this result provides very strong evidence that some trace gas or vapour X in the air is involved in UV nucleus formation.

Correlation of Z' and U :

There was a significant correlation between Z' the outdoor nucleus concentration, and U, the sulphur dioxide concentration in the outdoor air. The correlation coefficient ρ had the value $\rho = 0.79$. This result was not unexpected, as both Z' and U vary with the general level of pollution in the air. Both the outdoor nuclei and the sulphur dioxide are probably mainly added to the atmosphere as a result of combustion processes.

Correlation of Z and Z' :

The value of the correlation between the UV nucleus concentration Z and the outdoor concentration Z' was 0.69.

Correlation of Z and relative humidity of the air:

The only other correlation which might be significant is the correlation between Z, the UV nucleus concentration, and the relative humidity of the outdoor air (item (20), in Table 7). The value of the correlation coefficient in this case was $\rho = 0.32$. It would seem therefore that UV nucleus formation might increase as the humidity of the air increases. In the plot of Z against U, in Fig. 21, two points, marked A and B, had unusually high values of Z for relatively low values of U. The relative humidity of the outdoor air, corresponding to these two points, had the two highest values recorded; 93% in the case of A, and 96% in the case of B. These unusually high values of Z, for the sulphur dioxide concentrations involved, may have been due to the high relative humidity of the air.

Other correlations:

Rather unexpectedly, no significant correlation was found to exist between Z, the UV nucleus concentration, and the inverse of the wind speed at the time of the experiment (item 15, in Table 7) or the inverse of the mean wind speed (item (16)). When wind speed was low, one would expect the pollution of the air to be heavier, than when wind speed was high. However any correlation may have been masked by variations in other factors, such as wind direction. McWilliams and Morgan[72], found that condensation nucleus concentrations, in Valentia, Ireland, a remote coastal village, were generally higher with calms, and decreased with increasing wind speeds.

The author found no significant correlation, either, between the trend of wind speed during an experiment (item 17), and the trend of UV nucleus concentration during the experiment.

No significant correlation was found between Z, the UV nucleus concentration or U the sulphur dioxide concentration in the air, and either rainfall in the last 3 hours before an experiment, or rainfall in the last 24 hours before an experiment. Indeed some relatively high measurements of sulphur dioxide concentration were made during heavy, continuous rain. It seems that heavy rain is not very efficient in removing trace amounts of sulphur dioxide from the atmosphere.

No significant correlation was found between Z, the UV nucleus concentration, and the number of hours of sunshine, on the day on which the experiment was carried out (item 21, in Table 7). Neither was there any significant correlation found between Z, and outdoor or room temperatures.

There was no obvious dependence of Z, the UV nucleus concentration, on the prevailing wind direction. This result was as expected since the Department of natural Philosophy lies near the centre of Edinburgh, so that wind coming from all directions would be polluted. The least polluted wind ought to have come, however, from the direction 45° of the compass (north-east), since it had blown over the North Sea before reaching Edinburgh. The lowest recorded value of U, the sulphur dioxide concentration in the air, 1.4 pphm, was measured when the wind during the experiment was from the direction 50° of the compass.

Conclusion:

It seems that some trace gas or vapour X in city air, whose concentration varies in a similar manner to the concentration of sulphur dioxide, is responsible for UV nucleus formation.

THE FORMATION OF UV NUCLEI IN A MIXTURE OF SULPHUR DIOXIDE, CYLINDER OXYGEN AND CYLINDER NITROGEN.

Due to the interesting relationship found in the last experiment between the concentration of UV nuclei formed in filtered outdoor air, and the sulphur dioxide concentration in that air, it was now decided to find out whether nuclei would be produced by UV irradiation of low concentrations of sulphur dioxide, in "pure air". The "pure air" used, was in fact a mixture of 79% nitrogen, and 21% oxygen, by volume. A cylinder was obtained, which contained 21% oxygen, 7 ppm sulphur dioxide, by volume, and the balance was nitrogen. This cylinder was filled by the suppliers, according to the author's specifications, and the mixture was analysed by the suppliers, after filling, and found to contain 7 ppm (or 700 pphm) sulphur dioxide. A second cylinder containing 21% oxygen and 79% nitrogen, by volume, was obtained from the same suppliers. The "pure air" in this cylinder was used to dilute the sulphur dioxide mixture in the first cylinder, to various extents, in order to achieve very low concentrations of sulphur dioxide, of the same order of magnitude as the concentrations found in the filtered atmospheric air, formerly used.

Arrangement of apparatus: The arrangement of apparatus used, is shown in Fig. 22. The gas from cylinder (1), which contains the 7 ppm sulphur dioxide, passed through a pressure reduction and regulating head, through a rotameter R_1, and was then diluted with the "pure air" from cylinder (2). The diluted gas then passed through a 1.2 micron pore size Millipore filter, into the

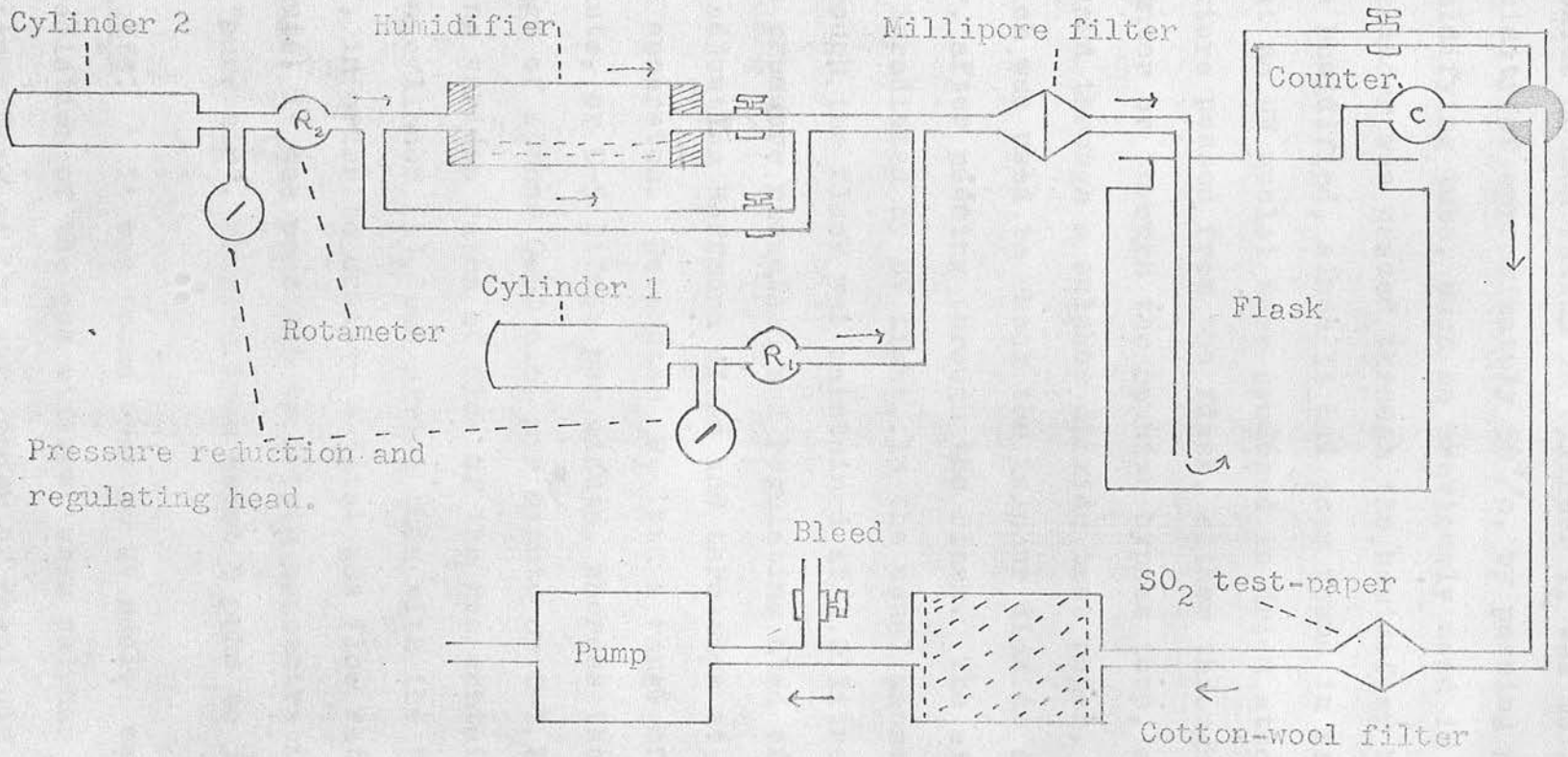


Figure 22: Arrangement of apparatus used in the experiment investigating UV nucleus formation in a mixture of sulphur dioxide, nitrogen and oxygen. Arrows show direction of gas flow.

borosilicate flask. The pure air used for diluting the sulphur dioxide concentration in cylinder I, was maintained at a relatively humidity of approximately 50°/o, by passing part of it through a humidifying tube, such as previously used in this work, and the remainder was passed through the humidifier bypass tube. The gas was humidified, since it had been found in previous experiments, that no UV nuclei were produced in dried atmospheric air. The gas mixture passed from the flask, either through the Nolan-Pollak counter or through the counter bypass tube, as usual. It then passed through a sulphur dioxide test paper, mounted as usual, which was used to check the sulphur dioxide concentration in the air, after passing through the flask. The air in the flask could be irradiated by UV light, in the usual manner. The total gas flow through the flask was maintained at 1.0 litre per minute, by using the pressure reduction and regulating head of both cylinders, and by adjusting Hoffmann clips and throttles at convenient points of the apparatus. Rotameter R_1 had a range of either 0-1 litre per minute, or 0-5 litres per minute, whereas the rotameter R_2 had a range of either 0-50 c.c. per minute or 0-1 litre per minute. By using various rates of flow of the gas containing sulphur dioxide, from cylinder (1), and mixing this with the "pure air" from cylinder (2), in order to achieve a total gas flow rate of 1.0 litre per minute, it was possible to obtain concentrations of sulphur dioxide, in "pure air", ranging from about 5 pphm to 350 pphm.

Results: It was found that no UV nuclei were produced by UV irradiation of the gas mixture, when sulphur dioxide concentrations were of the same order of magnitude as the concentrations

of sulphur dioxide measured in atmospheric air in previous experiments. Even when the sulphur dioxide concentration was 350 pphm, steady state nucleus concentration, in the dynamic method of irradiation, at a total gas flow rate of 1.0 litre per minute, was only about 55 per c.c. The sulphur dioxide concemtration was calculated from the amount of dilution of the gas from cylinder (1), which was assumed to contain 7 ppm sulphur dioxide. A sulphur dioxide concentration of 350 pphm was obtained by mixing a 500 c.c./min. flow rate of the gas from cylinder (1), with a 500 c.c./min. flow rate of "pure air" from cylinder (2).

It therefore seemed that sulphur dioxide in "pure air", at concentrations which were of the same order of magnitude as those found in Edinburgh air, in previous experiments, did not form condensation nuclei on irradiation with ultraviolet light, under the experimental conditions used.

UV Irradiation of atmospheric air with added sulphur dioxide:

It was now thought that some other trace gas, present in atmospheric air, but absent in the "pure air" used, in the last experiment, might be needed in addition to sulphur dioxide, in order to lead to UV nucleus formation. For this reason it was decided to dilute the gas containing sulphur dioxide, from cylinder (1), with atmospheric air which was relatively pure, instead of the "pure air" used in the last experiment. The arrangement of apparatus used in the last experiment and illustrated in Fig. 22, was slightly modified. Instead of passing "pure air" from cylinder (2), and mixing it with gas from cylinder (1), outdoor air was now used for this

dilution. The outdoor air was drawn in as usual, and mixed with the gas from cylinder (1). The gas mixture was now passed through the Millipore filter into the flask. A pump was connected in the air line, after the sulphur dioxide test paper, in Fig. 22, in order to draw the gas mixture through the flask. The outdoor air was not humidified before mixing with the gas containing sulphur dioxide, as it was judged to contain sufficient water vapour. As in the previous experiment various concentrations of sulphur dioxide were achieved, by using various amounts of dilution of the gas from cylinder (1).

Results:

The outdoor air used in these experiments was relatively pure. The experiments were carried out on three consecutive days in July. When filtered outdoor air was used, without any addition of gas from cylinder (1), there was no UV nucleus formation, indicating that sulphur dioxide concentration in the outdoor air itself was less than about 2.0 pphm. However, when a flow rate of 50 c.c. per minute of the gas from cylinder (1) was used, together with a flow rate of 950 c.c. per minute of outdoor air, there was copious production of UV nuclei. Fig. 23 shows a plot of the UV nucleus concentration Z, against time of irradiation T, in the dynamic method, used at the flow rate of 1.0 litre per minute. Z was measured at three minute intervals. The flask had been flushed with about ten times its volume of the gas mixture, as usual, before commencement of irradiation. The pattern of UV nucleus production was

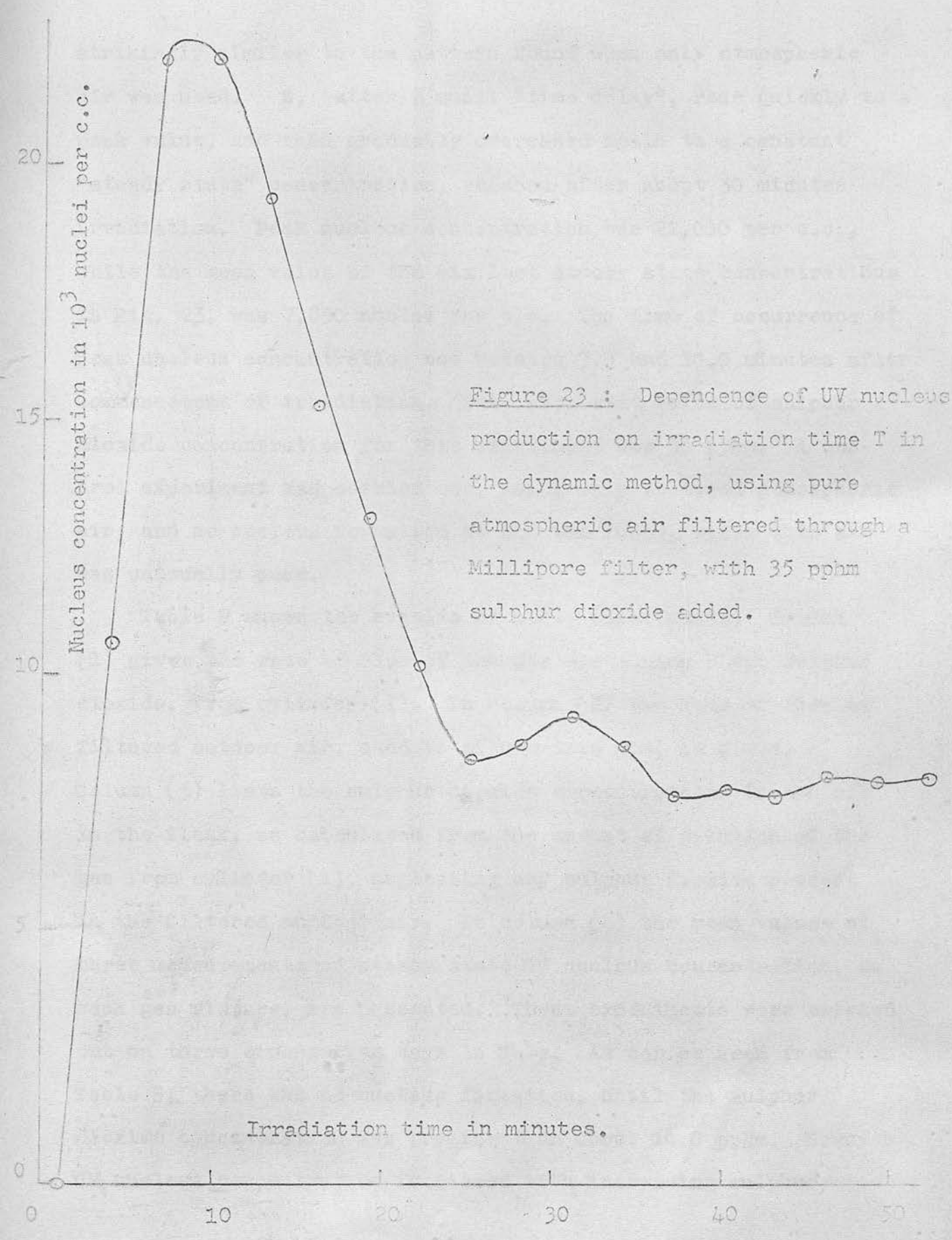


Figure 23 : Dependence of UV nucleus production on irradiation time T in the dynamic method, using pure atmospheric air filtered through a Millipore filter, with 35 pphm sulphur dioxide added.

strikingly similar to the pattern found when only atmospheric air was used. Z, after a small "time delay", rose quickly to a peak value, and then gradually decreased again to a constant "steady state" concentration, reached after about 30 minutes irradiation. Peak nucleus concentration was 22,000 per c.c., while the mean value of the six last steady state concentrations in Fig. 23, was 7,850 nuclei per c.c. The time of occurrence of peak nucleus concentration was between 7.0 and 10.0 minutes after commencement of irradiation. The calculated value of sulphur dioxide concentration for this experiment was 35 pphm. A control experiment was carried out, using only filtered atmospheric air, and no nucleus formation at all was found, since this air was unusually pure.

Table 9 shows the results of other experiments. Column (1) gives the rate of flow of the gas containing 7 ppm sulphur dioxide, from cylinder (1). In column (2) the rate of flow of filtered outdoor air, used to dilute this gas, is given. Column (3) lists the sulphur dioxide concentrations in the air in the flask, as calculated from the amount of dilution of the gas from cylinder (1), neglecting any sulphur dioxide present in the filtered outdoor air. In column (4) the mean values of three measurements of steady state UV nucleus concentration, in each gas mixture, are presented. These experiments were carried out on three consecutive days in July. As can be seen from Table 9, there was no nucleus formation, until the sulphur dioxide concentration was greater than about 14.0 pphm. However UV nucleus concentration increased with increasing sulphur

TABLE 9

UV nucleus formation in a mixture of sulphur dioxide and filtered atmospheric air.

Flow rate of gas from cylinder (1) in c.c. per minute	Flow rate of atmospheric air in c.c. per minute	Calculated SO_2 concentration in pphm	UV nuclei Z in nuclei/c.c.
0	1,000	0	0
20	980	14.0	0
25	975	17.5	2,390
40	960	28.0	6,290
50	950	35.0	7,850
50	950	35.0	11,200
100	900	70.0	12,000
150	850	105.0	18,900
200	800	140.0	156,000
500	500	350.0	211,000

dioxide concentration, reaching a value of 211,000 per c.c for a sulphur dioxide concentration of 350 pphm. This increase with sulphur dioxide concentration was not very regular, and it seemed that similar sulphur dioxide concentrations gave different values of Z, on various days. Thus, Z for a dulphur dioxide concentration of 35.0 pphm was 11,200 one day, and 7,850 the next day.

Comparison of calculated and measured values of sulphur dioxide concentration:

The values of the sulphur dioxide concentrations used were measured, on two occasions, using the ammoniacal zinc nitroprusside test paper method. Due to the relatively high sulphur dioxide concentrations sometimes used, the method had to be altered, as regards the length of the sampling period used. In the two tests made, the calculated values of sulphur dioxide concentrations were 35 pphm and 350 pphm, while the measured values were 22.2 pphm and 464 pphm respectively. Agreement was therefore not very good, but both estimates of the sulphur dioxide concentration, were at least of the same order of magnitude. Disagreement of the two methods may be due to a number of factors:

(1) The sulphur dioxide concentration in the gas coming from cylinder (1) might not have been 7 ppm all the time.

(2) The gas had passed through the flask, and had been irradiated, when the sulphur dioxide concentration was measured using the ammoniacal zinc nitroprusside test paper method. Some sulphur

dioxide may have been absorbed in the apparatus, and some was probably consumed in the photochemical reaction leading to UV nucleus formation.

(3) The test paper method could not always be used in the standard way, due to the unusually high sulphur dioxide concentrations sometimes achieved.

This comparison suggests that the test paper method gives values of sulphur dioxide concentrations, which are at least of the right order of magnitude. The sulphur dioxide concentrations in other experiments of the present series were not measured, using the test paper method, since there was not sufficient time available.

Agreement of results with those of other workers:

Hoppe[31] found that when he added sulphur dioxide to filtered atmospheric air, that there was a great increase in the number of UV nuclei formed on irradiation. He added sulphur dioxide concentrations ranging from about 1 pphm to about 9 pphm, and found that the concentration of UV nuclei produced was roughly proportional to the square of the sulphur dioxide concentration.

Discussion of results:

The results of these experiments offer very strong evidence that sulphur dioxide is involved in the formation of UV nuclei, in atmospheric air. It seems that sulphur dioxide and some other trace gas or vapour, present in city air, take part in a photochemical reaction leading to UV nucleus formation. Possible reaction-partners for sulphur dioxide, will be discussed in the next section.

The concentration of sulphur dioxide causing the formation of a given steady state concentration of UV nuclei in these experiments, was of the same order of magnitude as the concentration of sulphur dioxide in filtered atmospheric air, causing the formation of a similar concentration of UV nuclei. Thus, a steady state concentration of 11,200 UV nuclei per c.c. were produced in these experiments in one mixture containing 35 pphm sulphur dioxide, whereas in filtered atmospheric air, a steady state UV nucleus concentration of 9980 per c.c. was produced when the sulphur dioxide concentration was 14.3 pphm, in a typical experiment, (see Table 7, page 141c). The lower rate of UV nucleus production observed in these experiments may be due to a number of causes, for example,

(a) the concentration of the reaction partner of the sulphur dioxide is probably low when the sulphur dioxide concentration in the untreated atmospheric air is low, as it was in these experiments. The rate of UV nucleus formation from these two trace gases, probably depends on the product of both their concentrations in the air.

(b) There was some uncertainty about the actual concentration of sulphur dioxide present in the air in these experiments (see page 158). It is possible that some of the sulphur dioxide in cylinder (1) may have been oxidized to sulphur trioxide by the oxygen in the cylinder, as the pressure of the gas mixture was very high, of the order of 120 times the atmospheric pressure.

Effect of dilution rate on concentration of the sulphur dioxide reaction partner:

It must be remembered that as the rate of dilution of the gas from cylinder (1) with atmospheric air, was decreased, in these experiments, that the concentration of the reaction partner of the sulphur dioxide in the irradiated gas mixture was also decreased, since the atmospheric air constituted a smaller proportion of the irradiated gas. The fall in UV nucleus production, due to this decrease in concentration of the reaction partner of the sulphur dioxide, would thus eventually be greater than the increase in UV nucleus production due to the increase in sulphur dioxide concentration, as the dilution of the gas from cylinder (1), with "pure air", was increased. This effect is probably illustrated by the relatively slow increase in steady state UV nucleus concentration, from 156,000 per c.c. to 211,000 per c.c., as shown in the results in Table 9, between the sulphur dioxide concentrations of 140 pphm and 350 pphm. When the sulphur dioxide concentration was 140 pphm, there were 200 c.c./min. of gas from cylinder (1) mixed with 800 c.c./min. of atmospheric air, whereas when the sulphur dioxide concentration was 350 pphm, there were 500 c.c./min. of gas from cylinder (1) mixed with 500 cc./min. of atmospheric air. Assuming that the concentration of the reaction partner of the sulphur dioxide in the atmospheric air was the same in both cases, its concentration in the mixture for irradiation for the sulphur dioxide concentration of 350 pphm would be only $^{5}/_{8}$ths of the concentration for the mixture with a sulphur dioxide concentration of 140 pphm.

Conclusion:

It seems that UV nuclei are formed in city air, due to a photochemical reaction between sulphur dioxide and some other trace gas or vapour present in city air. The nuclei are possibly formed due to a chemical supersaturation of the air with a product of this reaction. The chemical supersaturation hypothesis has already been discussed in this work.

THE SPECIFIC ABSORPTION RATE OF SULPHUR DIOXIDE FOR THE UV RADIATION UNDER THE STANDARD EXPERIMENTAL CONDITIONS

Since it seems clear that sulphur dioxide is involved in the reaction leading to UV nucleus formation, the absorption of the UV radiation by sulphur dioxide in the air in the flask is now examined, theoretically.

The Specific Absorption Rate:

The specific absorption rate k_a is defined as the average fraction of molecules of absorbent, receiving photons per unit time. The value of k_a for a system such as existed in the author's experiments, where an absorbing gas is mixed at a low concentration with a non-absorbing gas (air), is given by the equation

$$k_a = I_a/c \qquad (1)$$

where I_a is the number of photons per second, absorbed in one c.c. of the gas, and c is the concentration of absorbent in the gas, expressed in molecules of absorbent, per c.c. of gas.

Absorption of ultraviolet radiation by sulphur dioxide:

The UV absorption spectrum consists of bands with sharp rotational structure, beginning at about 3950A and increasing to a maximum at about 2850A. The absorption above 3400A is very weak, and may be neglected.

Calculation of the Specific Absorption Rate:

For radiation varying in wavelength λ and in intensity, the specific absorption rate k_a is given by the following summation, taken over all values of λ,

$$k_a = \Sigma 2.303\ \alpha_\lambda\ j^{-1}\ J_\lambda \qquad (2)$$

where α_λ is the decadic absorption coefficient of the absorbent (sulphur dioxide), for light of wavelength λ, and J_λ is the photon flux in photons per cm^2 per sec, in the small wavelength range $\Delta\lambda$, centred on λ. A conversion factor j is used, to change α_λ to units corresponding to the units of concentration of absorbent, which is expressed in molecules per c.c. of gas. In order to calculate the value of k_a of sulphur dioxide, for the experimental conditions used by the author, it is necessary to find out first of all the values of J_λ for various wavelength intervals, for the ultraviolet light irradiating the air in the borosilicate flask. It is also necessary to know the values of α_λ the decadic absorption coefficient of sulphur dioxide, for the the values of λ on which these wavelength intervals are centered.

Evaluation of the J_λ's:

The spectrum of the Phillips MLU 300w ultraviolet lamp used, is partly a line spectrum and partly a continuous spectrum. The spectral energy distribution of the light, according to the manufacturers, at a point on the main axis of the lamp (see Fig. 24), 50 cm. from the front of the lamp, has already been given in Table 1, page 17. The total light intensity at this point is called I_o.

The average intensity of the UV light irradiating the air in the flask:

An estimate of the average total intensity of the UV light irradiating the air in the borosilicate flask was found as follows, in terms of I_o. The absorption of the UV light by the borosilicate glass of the flask is neglected for the moment, but it will be dealt with at a later stage. The intensity of the UV light was calculated in units of I_o for the points of intersection of the main axis of the lamp and the inside walls of the flask, and also half-way between these points, at the point of intersection of the main axis of the lamp, and the vertical axis of the flask. These points A, B and C respectively, are shown schematically in Fig. 24. It was assumed that the intensity of the UV light along the main axis of the lamp, obeyed the inverse square law. The distance between the lamp front and the nearest point of the flask was taken to be 15.7 cm., the standard separation used in the author's experiments. The mercury arc itself was about 8 cm. behind the lamp front. The average intensities of the UV light, passing through the planes inside the flask, perpendicular to the main axis of the lamp, at the points A, B and C, were now found. This was done, by using the curve shown in Fig. I, which gives the irradiation pattern of the lamp in a plane perpendicular to the main axis of the lamp, at a distance of 50 cm from the front of the lamp. This curve was supplied by the manufacturers. From these three values of UV light intensity, the average total intensity of the UV light of all wavelengths, irradiating the air in the flask, was estimated to be about 2.2 I_o. It must be

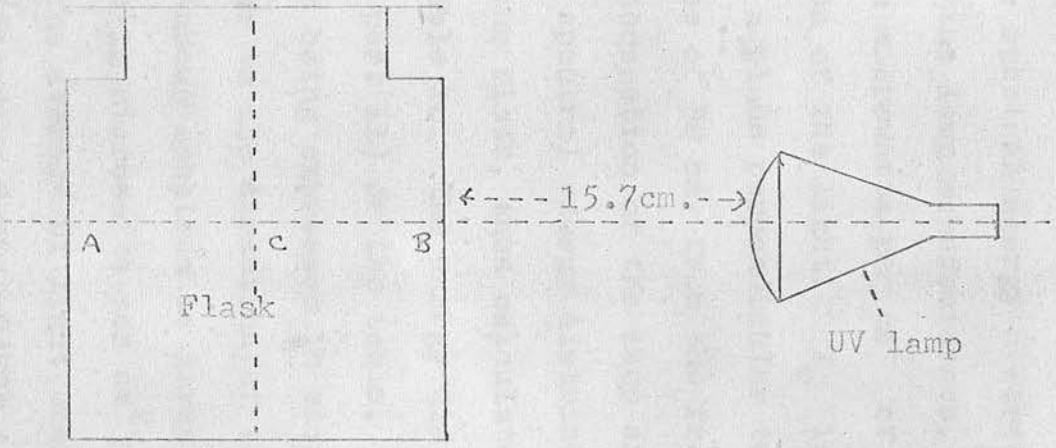


Figure 24 : The points A, B, and C which are mentioned on page 165.

remembered that the absorption of the UV light by the walls of the flask, has thus far been completely neglected.

The approximate spectral energy distribution of the UV light irradiating the air in the flask was found by multiplying by 2.2 the light energies for various wavelengths and wavelength intervals, as given in Table I, for a total UV light intensity of I_o. The spectral energy distribution data in Table I was provided by the lamp manufacturers, and the light energies are expressed in microwatts per cm^2 of a surface perpendicular to the direction of the light. I_o is the total intensity of the UV light on a plane perpendicular to the main axis of the lamp, at a distance of 50 cm. from the front of the lamp; at the point of intersection of the lamp axis and the plane. The approximate spectral energy distribution of the UV light, irradiating the air in the flask, thus calculated, is given in the second column of Table 10. The energy distribution of the line spectrum is given in part (1) of the table, the energy for each line of the spectrum being expressed in microwatts per cm^2 of a surface perpendicular to the direction of the light. The energy distribution of the continuous spectrum is given in part (2) of Table 10, and is expressed in microwatts per cm^2 per 100A interval of the spectrum. The average UV light energy is given for each 100A interval, centred on 2750A, 2850A etc. up to 4050A.

Transmission of the UV light by the borosilicate glass of the flask:

The effect of the absorption of UV light by the walls of the flask must now be taken into account, in order to evaluate the average flux of photons of UV light of different wavelengths, passing through the air in the flask.

TABLE 10

Spectral energy distribution and decadic absorption coefficients for sulphur dioxide, for the UV light irradiating the air in the flask.
Part (1): The line spectrum

λ in Angstrom units	Light energy in $\mu W/cm^2$	Percentage transmission	J_λ in 10^{13} photons $cm^2/sec.$	a_λ in litre/ mole/cm.
2804	22	0	0	
2894	22	6	0.19	157
2967	132	20	3.94	139
3025	374	33	18.8	102
3130	1160	57	105.0	32
3341	154	83	21.5	2.2
3655	2930	89	479.0	-
4047	924	89.5	168.0	-
4358	1720	89.5	337.0	-
5461	2130	90.5	531.0	-
5780	2090	90.5	550.0	-

TABLE 10 (cont.)

Part (2): The continuous spectrum

λ in Angstrom units	Light energy in $\mu W/cm^2$/ 100A	Percentage transmission	J_λ in 10^{13} photons cm^2/sec./100A	α_λ in litre/ mole/cm.
2750	22	0	0	
2850	44	2	0.13	160
2950	66	16	1.57	145
3050	88	38	5.13	80
3150	110	61	10.6	25
3250	110	74	13.3	7
3350	110	83	15.4	2
3450	88	86	13.1	0.5
3550	66	88	10.4	-
3650	66	89	10.8	-
3750	44	89	7.39	-
3850	44	89	7.59	-
3950	22	89	3.99	-
4050	22	89.5	4.02	-

The third column of Table 10 lists the values of the percentage transmission of the ultraviolet light of the various wavelengths listed in the first column, by borosilicate glass of similar manufacture to the glass in the borosilicate flask, and of thickness 6.15 mm. These values were calculated from a transmission curve provided by the manufacturers of the borosilicate flask, with the kind permission of the British Glass Industry Research Association, who made the actual determinations. According to the manufacturers, there are slight variations from time to time on current manufactured borosilicate glasses, but this curve is fairly representative. The transmission curve is reproduced in Fig. 25, for wavelengths from 2700A to 4500A. It may be noticed that the borosilicate glass does not transmit UV light of wavelength less than about 2800A. The percentage transmission increases from 2°/o at 2850A to 38°/o at 3050A, to 88°/o at 3550A, and then remains almost constant for the rest of the visible spectrum.

The thickness of the borosilicate glass in the flask was not uniform, but was greater at the bottom of the flask than at the top. The average of three measurements of thickness of the side walls of the flask, at the top, middle and bottom of the flask was 6.10 mm. Therefore within the limits of experimental error, the percentage transmissions calculated from the transmission curve for 6.15 mm borosilicate glass may be used, for the glass of the flask.

The approximate average spectral energy distribution of the UV light reaching the air in the flask, through the borosilicate glass, is found by multiplying the light energy for each wavelength in the first column of Table 10, by the percentage transmission for that wavelength. This spectral energy distribution

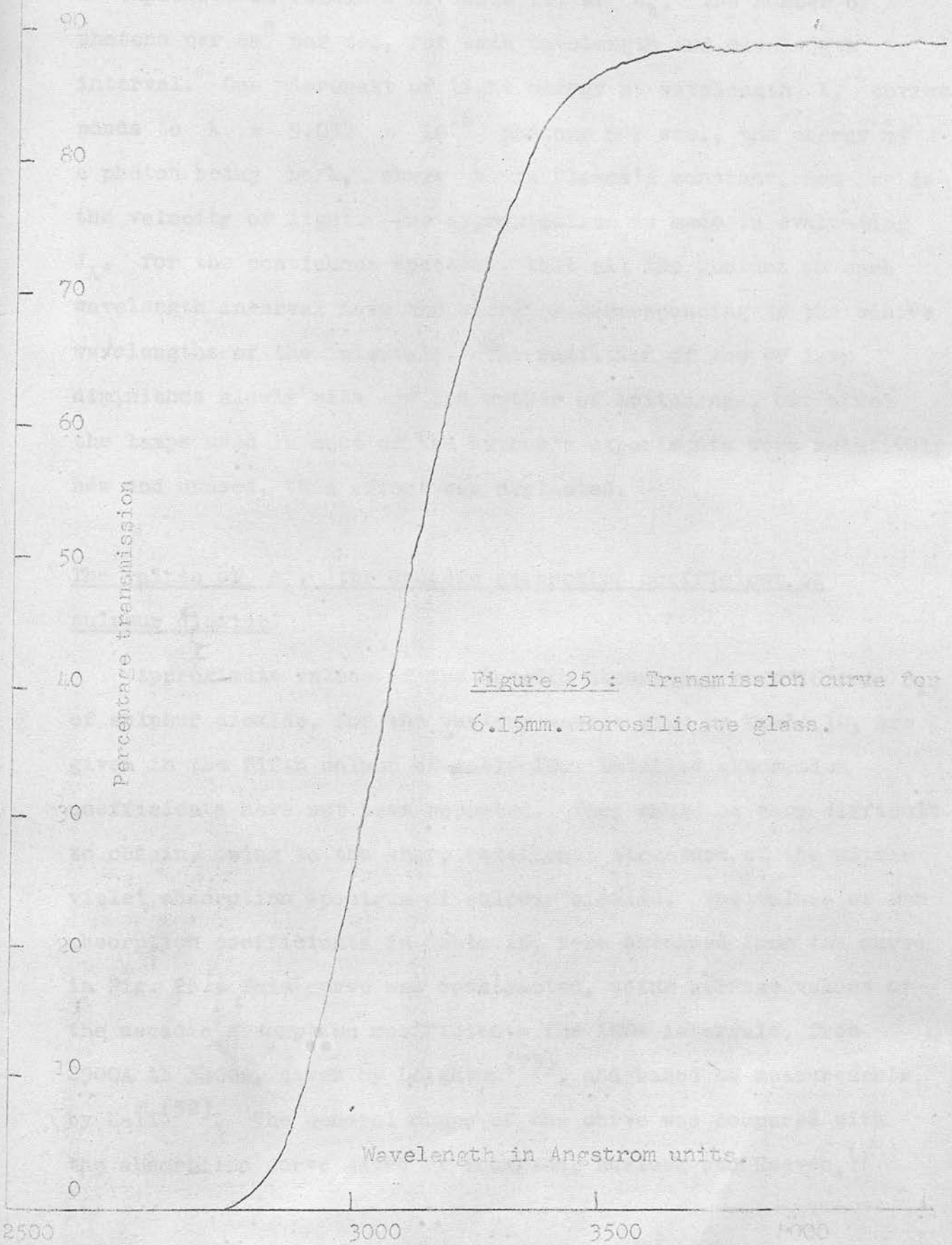


Figure 25 : Transmission curve for 6.15mm. Borosilicate glass.

is expressed in column 4 of Table 10, as J_λ, the number of photons per cm^2 per sec, for each wavelength and wavelength interval. One microwatt of light energy at wavelength λ, corresponds to $\lambda \times 5.034 \times 10^{16}$ photons per sec., the energy of a photon being hc/λ, where h is Planck's constant, and c is the velocity of light. The approximation is made in evaluating J_λ, for the continuous spectrum, that all the photons in each wavelength interval have the energies corresponding to the centre wavelengths of the intervals. The radiation of the UV lamp diminishes slowly with age and number of switchings, but since the lamps used in most of the author's experiments were relatively new and unused, this effect was neglected.

The values of α_λ, the decadic absorption coefficient of sulphur dioxide:

Approximate values of the decadic absorption coefficient α_λ, of sulphur dioxide, for the various wavelengths in Table 10, are given in the fifth column of table 10. Detailed absorption coefficients have not been reported. They would be very difficult to obtain, owing to the sharp rotational structure of the ultraviolet absorption spectrum of sulphur dioxide. The values of the absorption coefficients in Table 10, were obtained from the curve in Fig. 26. This curve was constructed, using average values of the decadic absorption coefficients for 100A intervals, from 2900A to 3400A, given by Leighton[73], and based on measurements by Hall[52]. The general shape of the curve was compared with the absorption curve given by Thompson, Harteck and Reeves,[74]

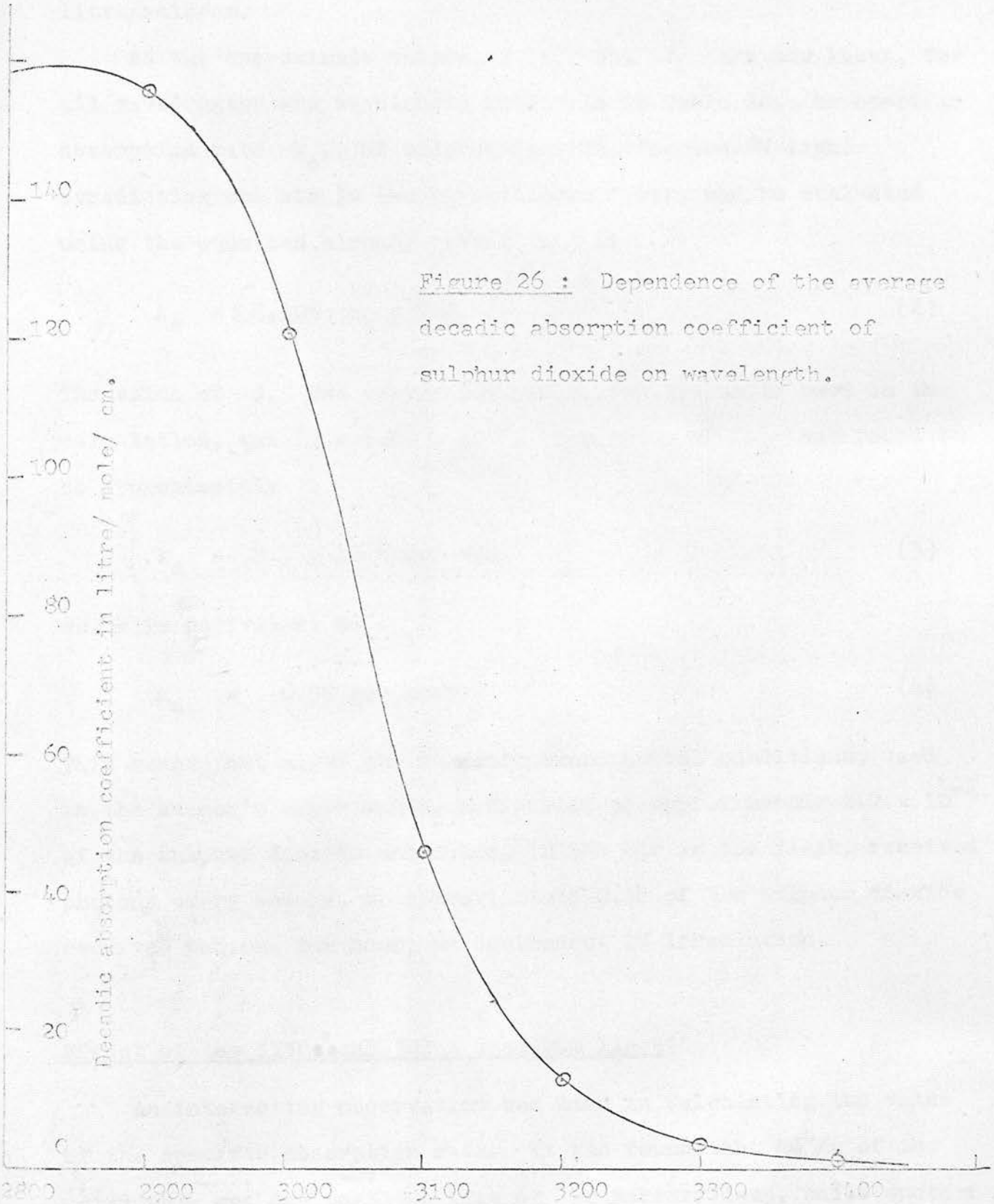


Figure 26 : Dependence of the average decadic absorption coefficient of sulphur dioxide on wavelength.

The decadic absorption coefficients in Table 10 are expressed in litre/mole/cm.

As the approximate values of α_λ and J_λ are now known, for all wavelengths and wavelength intervals in Table 10, the specific absorption rate k_a, of sulphur dioxide, for the UV light irradiating the air in the borosilicate flask, may be evaluated using the equation already given, that is

$$k_a = \Sigma 2{,}303 \ \alpha_\lambda \ j^{-1} \ J_\lambda \qquad (2)$$

The value of j, the conversion ratio, for the units used in the calculation, was $j = 6.02 \times 10^{20}$. The value of k_a was found to be approximately

$$k_a = 2.7 \times 10^{-4} \text{ per sec.} \qquad (3)$$

which is equivalent to

$$k_a = 0.98 \text{ per hour} \qquad (4)$$

This means that under the standard experimental conditions, used in the author's experiments, a fraction of approximately 2.7×10^{-4} of the sulphur dioxide molecules, in the air in the flask, received photons every second, or approximately 0.98 of the sulphur dioxide received photons per hour, on continuous UV irradiation.

Effect of the 3130A and 3025A spectrum lines:

An interesting observation was made in calculating the value of the specific absorption rate. It was found that 48°/o of the total rate was due to the 3130A line of the mercury lamp, while another

28°/o was due to the 3025A line. These two lines, together were therefore responsible for about 76°/o of the total specific absorption rate. This means that 76°/o of the total amount of any photochemical reaction, involving sulphur dioxide, and due to the absorption of photons by the sulphur dioxide would be caused by the light energy in these two spectrum lines.

The Effect of the absorption of UV radiation on sulphur dioxide:

The sharp rotational structure in the absorption spectrum of sulphur dioxide is evidence that the molecule is not photo-dissociated by solar radiation in the lower atmosphere, or by near ultra violet radiation. This is confirmed by the energy requirements of the possible dissociation processes. According to Leighton[73], the estimated bond dissociation energy for the reaction

$$SO_2 \qquad SO + O$$

is 135 kcal/mole, which corresponds to the einstein at 2100A. Dissociation into a sulphur atom and an oxygen molecule would also require 135 kcal/mole, and dissociation into a sulphur atom and two oxygen atoms would require 235 kcal/mole. The energy of the einstein in the region of solar radiation, which is absorbed by sulphur dioxide, and in the region of UV radiation irradiating the air in the flask, in the author's experiments, ranges from about 85 to 95 kcal/mole. Hence, it falls short of the requirements for dissociation. Therefore, the primary photochemical processes following absorption of solar radiation, or near UV radiation,

such as used in the author's experiments, must involve excited sulphur dioxide molecules, rather than dissociation.

The specific absorption rate is a measure of the rate at which sulphur dioxide molecules are excited by the given UV radiation. The rate of a photochemical reaction involving these excited sulphur dioxide molecules, is therefore a function of this specific absorption rate. Since there is very strong evidence from the author's experiments, that the formation of UV nuclei is caused by such a photochemical reaction, the rate of formation of these UV nuclei in filtered city air, is probably a function of the specific absorption rate and the sulphur dioxide concentration, and should increase for a particular sulphur dioxide concentration, as the specific absorption rate increases. Therefore the specific absorption rate, k_a, is probably a measure of the UV nucleus forming power of a given UV radiation.

Comparison of the Specific Absorption rate of sulphur dioxide, for ultraviolet light, under the standard experimental conditions, and for natural sunshine:

Since the specific absorption rate of sulphur dioxide is probably a measure of the UV nucleus forming power of a given UV radiation, it was thought interesting to compare the specific absorption rate of sulphur dioxide, for the UV radiation irradiating the air in the flask, under standard experimental conditions, and for solar radiation in the open atmosphere.

Table 11 is taken from Leighton[73], and gives the specific absorption rate k_a of sulphur dioxide for direct and indirect solar ultraviolet radiation under a clear sky, for different solar

TABLE 11

The specific absorption rates of sulphur dioxide for direct and indirect solar radiation from a clear sky

Solar zenith angle (Z)	k_a	
	sec^{-1}	$hour^{-1}$
0	2.6×10^{-4}	0.94
20	2.4×10^{-4}	0.86
40	1.7×10^{-4}	0.62
60	0.7×10^{-4}	0.26
80	0.1×10^{-4}	0.04

zenith angles, in units of sec^{-1} and $hour^{-1}$.

The value of 2.7×10^{-4} per sec. found for k_a, for the author's experimental conditions may be seen to be almost the same as the value of k_a for direct and indirect radiation from the sun at the zenith, in a clear sky. The solar zenith angle at midday in Edinburgh, varies from $32\frac{1}{2}^{o}$ at the summer solstice to 56^{o} at the autumn and spring equinoxes, and to $79\frac{1}{2}^{o}$ at the winter solstice. It is found, using Table 11, that the value of $k_a = 2.0 \times 10^{-4}$ per sec. at the summer solstice, is about twenty times as large as the value at midday at the winter solstice, when $k_a = 0.1 \times 10^{-4}$ per sec.

The specific absorption rate of sulphur dioxide, for the UV radiation irradiating the air in the flask, in the author's experiments, is about 1.35 times the specific absorption rate for natural sunshine, from a clear sky, at midday at the summer solstice, and 27.0 times the specific absorption rate for natural sunshine, from a clear sky at midday at the winter solstice. Since the specific absorption rate of sulphur dioxide, for natural sunshine is of the same order of magnitude as the specific absorption rate for the UV radiation used in the author's experiments, it seems fair to apply the results of these experiments to the atmosphere, and to suggest that a large concentration of UV nuclei should be produced in a sufficiently polluted atmosphere, when the solar radiation is strong enough.

In winter, the pollution levels of the Edinburgh air are normally sufficiently high to cause a copious production of

condensation nuclei, with suitable ultraviolet radiation. This has already been shown in this work, on pages 145-148. However, in winter, the value of the specific absorption rate of sulphur dioxide, for the weak solar radiation during winter in Edinburgh, is probably not high enough to give a very significant rate of formation of nuclei. However, Aitken[11] noticed the formation of such nuclei, during the winter in Falkirk, not far from Edinburgh. These nuclei become visible as haze, under suitable calm, humid conditions. It seems therefore that the solar ultraviolet radiation - even in winter - is strong enough to form some UV nuclei in a heavily polluted atmosphere.

On the other hand, in summer, the nucleus forming UV radiation is present in much higher quantity, but the pollution level of the Edinburgh air is almost invariably too low in summer to cause UV nucleus formation. This seems a fortunate occurrence, because the results of the author's experiments suggest that a very large concentration of condensation nuclei would be formed if high pollution levels coincided with strong sunshine. The formation of such a large concentration of UV nuclei would probably cause a thick visible haze to appear, under suitable conditions.

Experimental investigation of the spectral distribution of the light from the UV lamp, using a UV spectrograph and a microdensitometer:

An independent investigation was made of the spectral energy distribution of the UV light from the UV lamp, before and after passing through the borosilicate glass of the flask, in order to check the percentage transmissions given in Table 10.

The spectrum of the UV light from the lamp was photographed, using an ultraviolet spectrograph. The distance from the lamp front to the spectrograph slit, which was on the main axis of the lamp, was 40 cm. Spectra were obtained for the UV light, after passing through 40 cm. of air and after passing through 40 cm. of air and the bottom of the borosilicate flask. Kodak B.10 plates were used for the spectrographs. The spectrographs were then analysed, using a Joyce Loebl double-beam recording microdensitometer. Figs. 27 and 28 show the microdensito meter recordings of the spectra of the UV light after passing through 40 cm. of air, the exposure times for the spectrographs being approximately 1 sec. and 5 sec. respectively. The lines of the mercury spectrum, down to the 2753A line inclusive, are present. Figs. 29 and 30 show the microdensitometer recordings of the spectrographs of the UV light, after it had passed through 40 cm. of air and the bottom of the borosilicate flask, the exposure times again being approximately 1 sec. and 5 sec. respectively. It may be noticed that none of the spectral lines below the 2967A line, were recorded. The percentage transmission of the spectral lines through the borosilicate glass of the flask, as calculated, approximately, from a comparison of the spectral

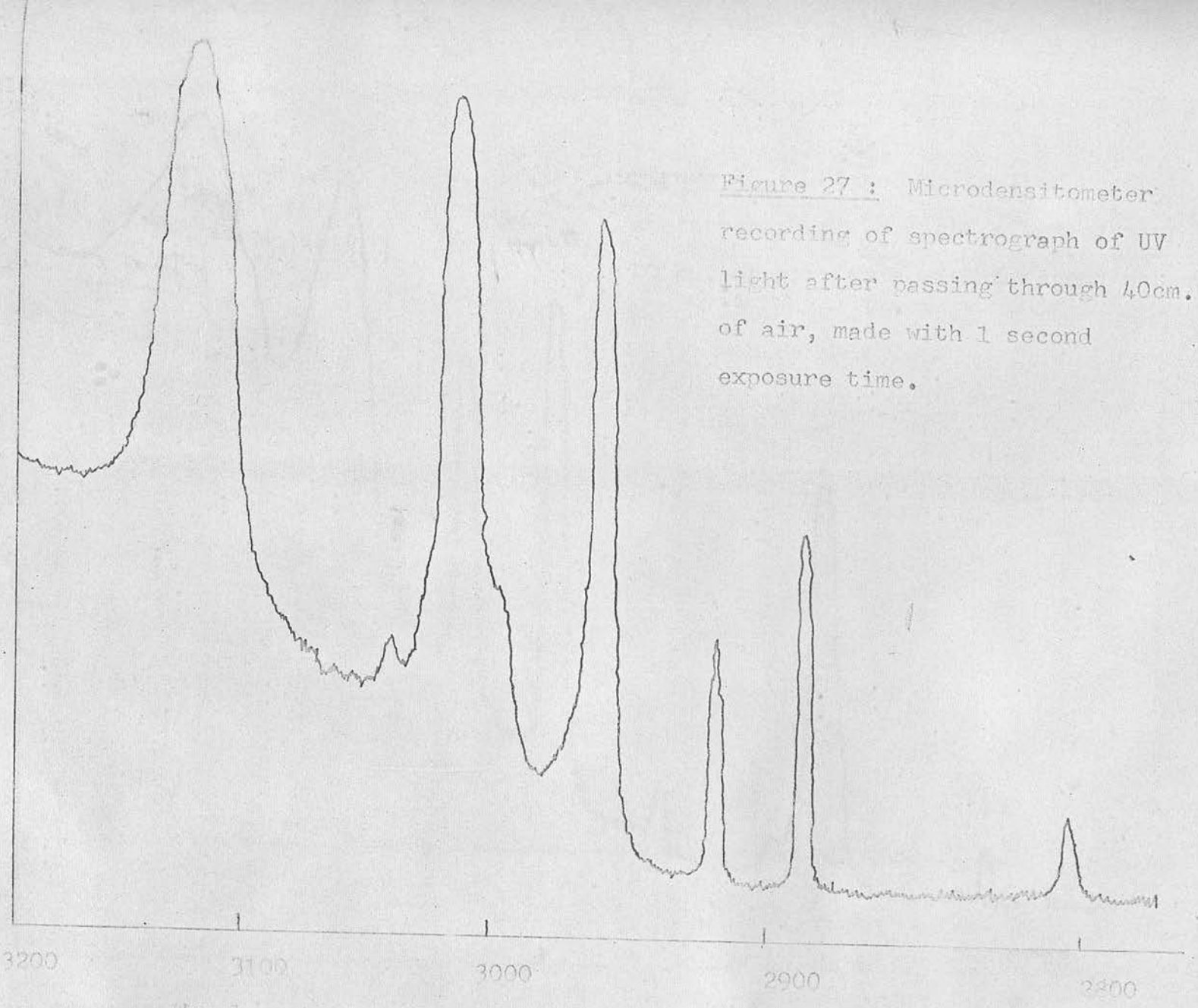


Figure 27 : Microdensitometer recording of spectrograph of UV light after passing through 40cm. of air, made with 1 second exposure time.

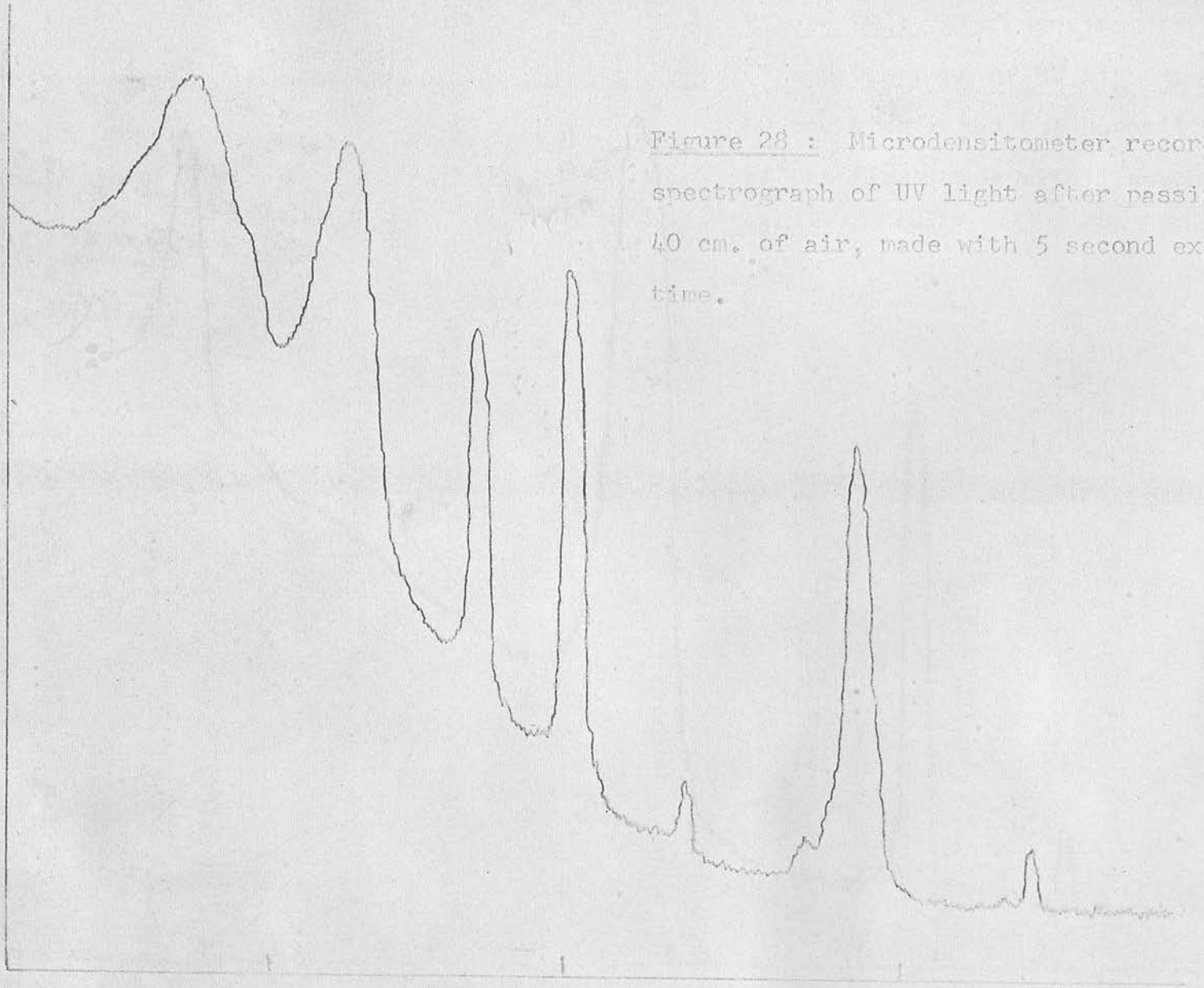


Figure 28 : Microdensitometer recording of spectrograph of UV light after passing through 40 cm. of air, made with 5 second exposure time.

wavelength in Angstrom units.

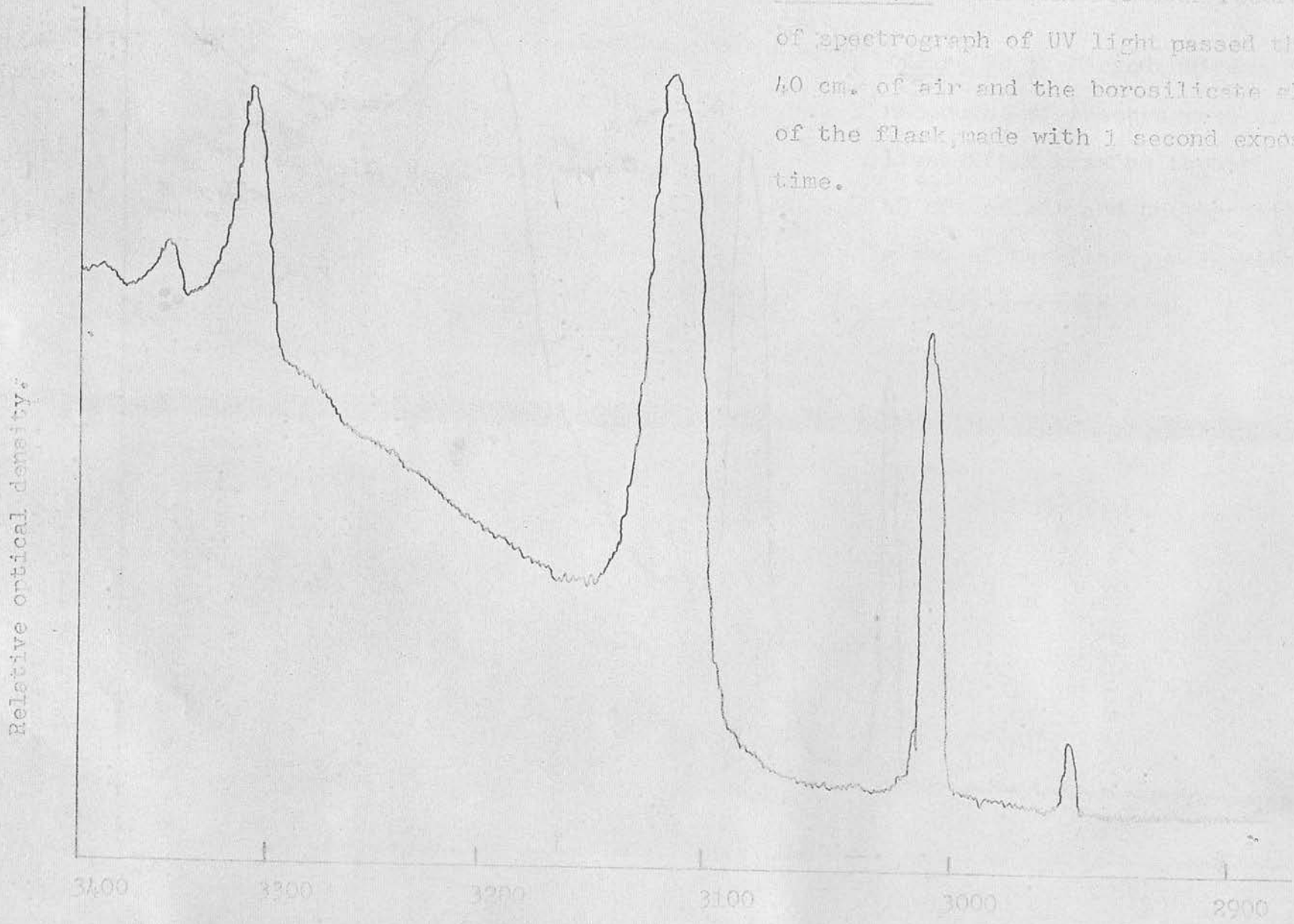


Figure 29 : Microdensitometer recording of spectrograph of UV light passed through 40 cm. of air and the borosilicate glass of the flask, made with 1 second exposure time.

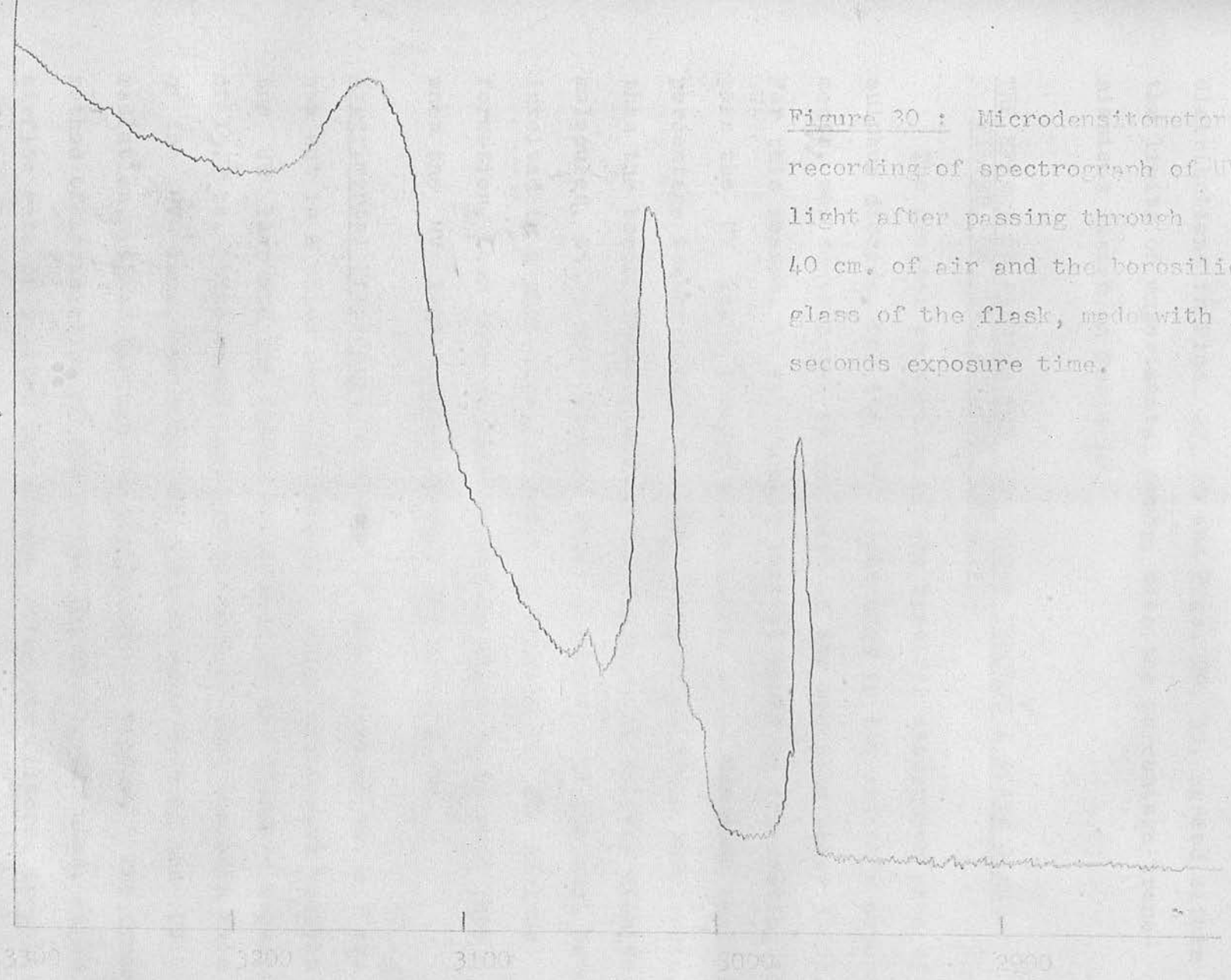


Figure 30 : Microdensitometer recording of spectrograph of UV light after passing through 40 cm. of air and the borosilicate glass of the flask, made with 5 seconds exposure time.

distributions in Figs. 27, 28 and Figs. 29, 30, agreed within the limits of experimental error, with the percentage transmissions listed in Table 10.

THE EFFECT OF PASSING THE UV LIGHT THROUGH A PLATE GLASS FILTER, ON UV NUCLEUS FORMATION:

The greater proportion of the specific absorption rate of sulphur dioxide, for the UV light used in the author's experiments, was contributed by the part of the spectrum below 3200A. For this reason, it was thought that it would be interesting to pass the UV light through plate glass, which has much smaller percentage transmissions for UV light below 3200A wavelength, than the borosilicate glass of the flask. If sulphur dioxide molecules, which were excited after absorption of photons, were involved in a photochemical reaction leading to UV nucleus formation, then this nucleus formation ought to be much less when the UV light passed through the plate glass.

Experimental Procedure: A window of dimensions 10 cm. x 7 cm. was cut in a thick cardboard shutter, which was placed between the UV lamp and the flask, which were at the standard separation of 15.7 cm. The window was positioned, so that the main axis of the UV lamp, and hence the most intense part of the UV radiation, passed through the centre of the window. The dynamic method of irradiation of the air in the flask, was used, at an airflow rate of 1 litre per minute, using air filtered through a 1.2 micron pore size Millipore filter. The mean value of UV nucleus concentration, after steady state nucleus concentration had been reached, was 440 per c.c.

A piece of plate glass, of uniform thickness 5.5 mm., was now placed in the window, covering the whole opening. UV nucleus concentration dropped gradually, reaching a mean value of zero, after 45 minutes.

Analysis of the spectral energy distribution of the UV light, after passing through the plate glass:

The spectral energy distribution of the UV light, after passing through 40 cm. of air and through the plate glass filter used above, was examined, using a UV spectrograph, and a microdensitometer, as described in the last section, on page 174. The microdensitometer recordings of the spectrographs made with approximately 1 sec. and 5secs. exposure times, are shown in Figs. 31 and 32. It is clear from these recordings, that very little of the UV light of wavelength less than 3200A, was transmitted by the plate glass. Figs. 31 and 32 were compared with Figs. 27 and 28, respectively, which show the microdensitometer recordings of the spectrographs of the UV light from the lamp, after passing through only 40 cm. of air, which were made with exposure times of approximately 1 sec. and 5 secs. From this comparison, approximate percentage transmissions of the plate glass, for the wavelengths of the spectral distribution of the UV light, from 2800A to 3400A, given in table 10, were obtained. It was found that the percentage transmission of the plate glass, for the 3130A line, was only a few percent, whereas the percentage transmission of borosilicate glass, for this line, was about 57°/o. It may be remembered that the 3130A line was responsible for 48°/o of the specific absorption rate of sulphur dioxide, for the UV light after passing through the borosilicate glass of the flask.

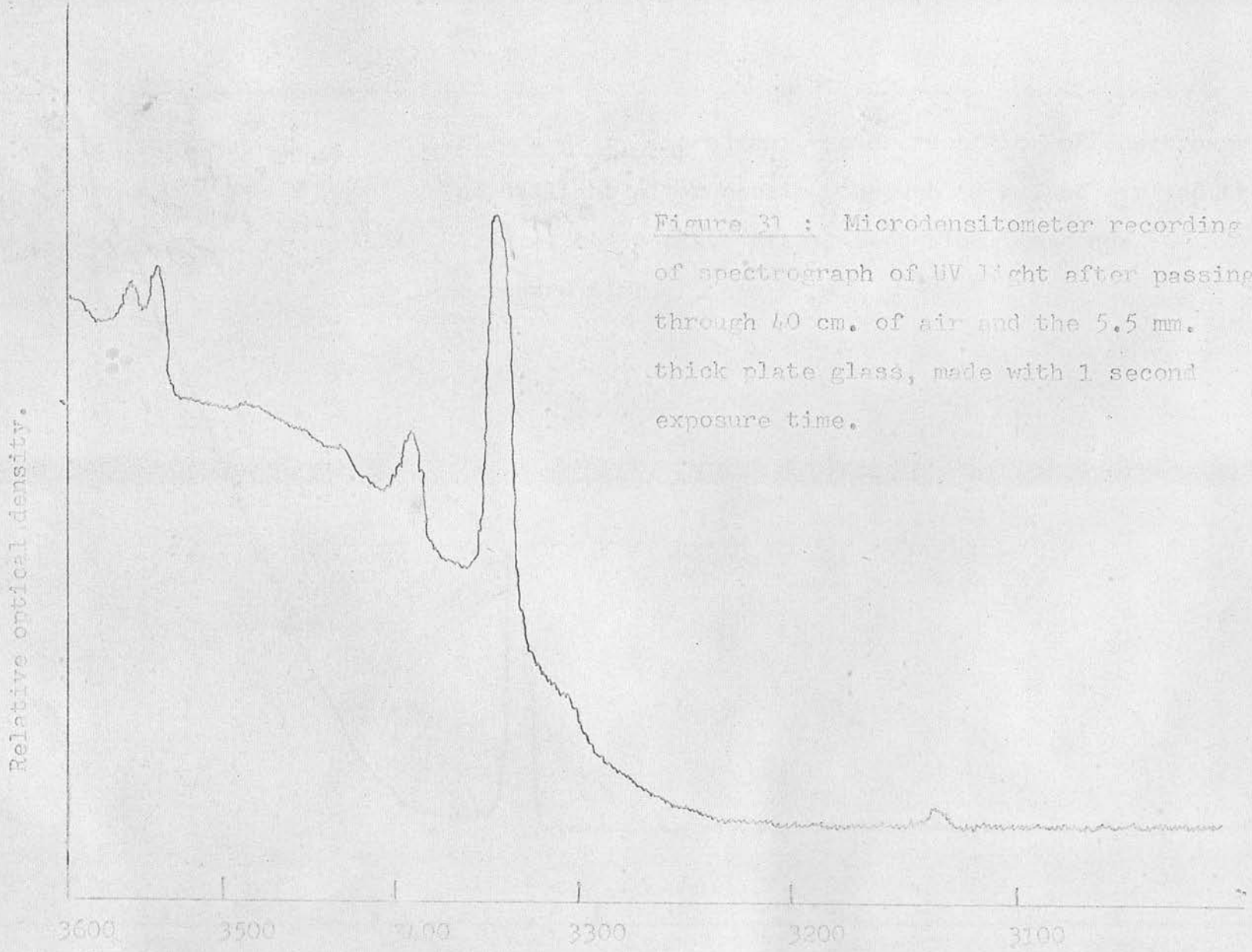
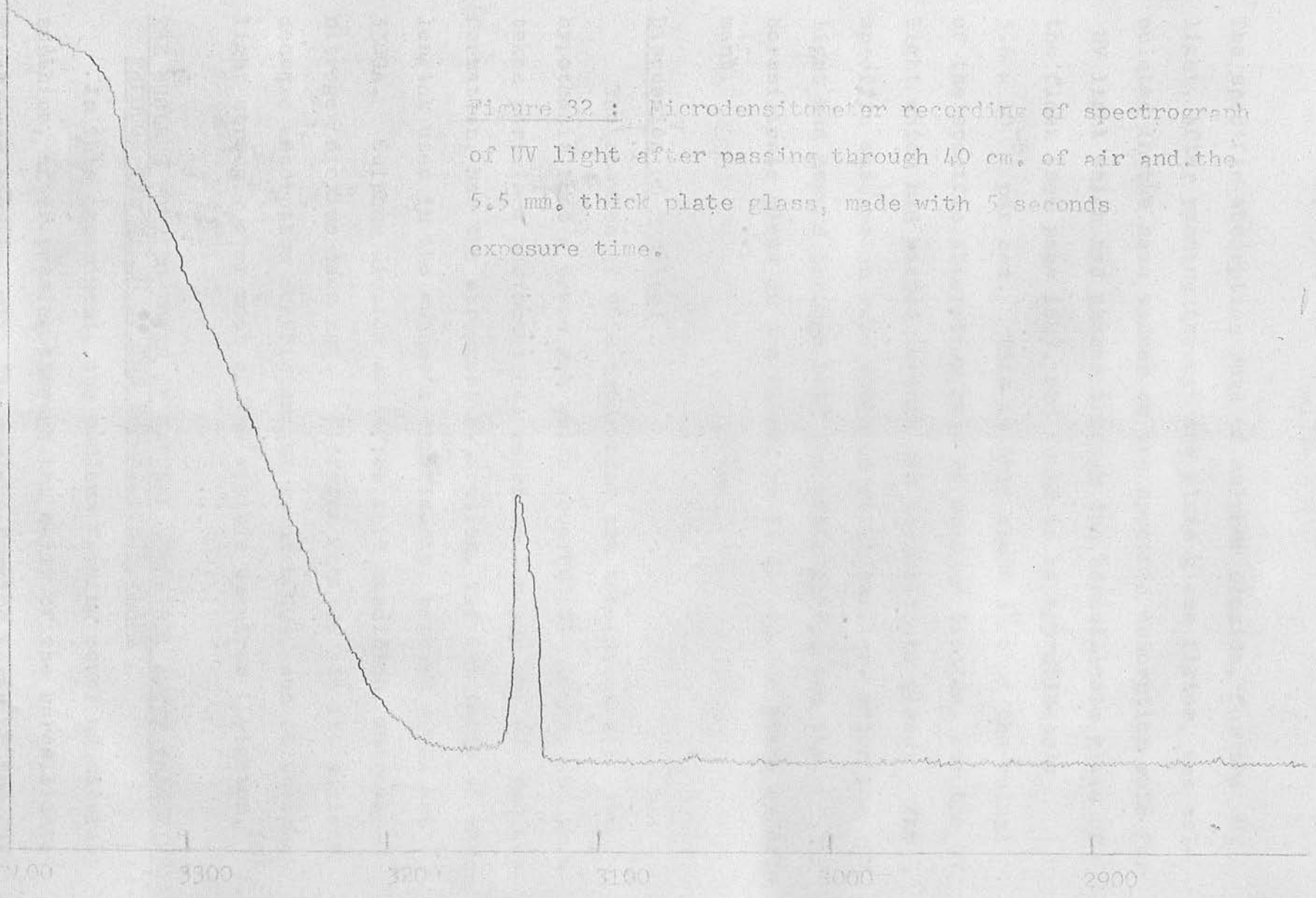


Figure 31 : Microdensitometer recording of spectrograph of UV light after passing through 40 cm. of air and the 5.5 mm. thick plate glass, made with 1 second exposure time.

Figure 32 : Microdensitometer recording of spectrograph of UV light after passing through 40 cm. of air and the 5.5 mm. thick plate glass, made with 5 seconds exposure time.



The specific absorption rate of sulphur dioxide, for the UV light, after passing through the plate glass filter, was calculated in the same manner as the specific absorption rate for UV light which had passed through the borosilicate glass of the flask (see page 164), and found to be approximately 3.6×10^{-6} per sec. This is only about 3°/o of the value of the specific absorption rate of sulphur dioxide, for the UV light which had passed through the borosilicate glass. The specific absorption rate would be still smaller, after the UV light had passed through both the plate glass, and the borosilicate glass of the flask, as it did in the above experiment.

Discussion of results:

The results of this experiment are consistent with the hypothesis that a trace gas which absorbs UV light, and then takes part in a photochemical reaction leading to UV nucleus formation, has the strongest absorption, for the range of wavelengths used in the author's experiments, between 2900A and 3300A. Sulphur dioxide satisfies this condition, whereas nitrogen dioxide does not. Nitrogen dioxide has its maximum decadic absorption coefficient at about 4000A, and it absorbs light strongly over most of the visible spectrum (Leighton,[6]).

THE NUCLEUS FORMING POWER OF NATURAL SUNSHINE, AFTER TRANSMISSION THROUGH THE WALLS OF THE BOROSILICATE FLASK

In this experiment, the nucleus forming power of natural sunshine, after passing through the walls of the borosilicate flask, was compared with the nucleus forming power of the UV light normally used. The dynamic method of irradiation was

employed, using air which had been filtered through a 1.2 micron pore size Millipore filter, at a flow rate of one litre per minute. The flask in its usual container, with its cooling fan, was placed near to a laboratory window, so that it could be exposed to natural sunshine. The UV lamp was used for irradiation, initially, and a steady state nucleus concentration was reached. The mean of three measurements of nucleus concentration was 4,700 per c.c. The UV lamp was now switched off, the cooling fan was removed, and the flask and the air passing through it, was irradiated with natural midday sunshine, shining through the open window. The zenith angle of the sun was estimated to be approximately 40^{o}. Nucleus concentration dropped gradually to zero, over the next 50 minutes. It must be remembered that it would take 50 minutes, approximately, to remove completely the nuclei that were already in the flask, since the flask would be flushed with only about 8 times its volume of air, in this time. The UV lamp was now switched on again, and nucleus production recommenced, increasing to a concentration of 3,280 nuclei per c.c. in 26 minutes.

Calculation of the specific absorption rate of sulphur dioxide, for the natural sunshine, after passing through the walls of the borosilicate flask:

The specific absorption rate of sulphur dioxide for the natural sunshine, after passing through the borosilicate glass of the flask, was calculated, as on page 164. The values of J_{λ} for equation (2), page 164, were calculated, by using the values for the photon flux distribution, of natural sunshine, for wavelength intervals of 100A, for a solar zenith angle of

40°, according to Leighton[6], and the values of the average percentage transmissions of borosilicate glass, for these wavelength intervals. The photon flux distribution given by Leighton, is for direct and sky solar radiation. The average values of the decadic absorption coefficient $a\,\lambda$, for these wavelength intervals, are also taken from Leighton[73]. The value of the specific absorption rate k_a was found to be about 1×10^{-4} per sec. for the direct and sky solar radiation. However, in the author's experiment, very little of the sky radiation reached the flask. Leighton[6] shows diagrammatically, that for a solar zenith angle of 40°, sky radiation below 3200A is approximately twice as intense as the direct radiation. Therefore, the specific absorption rate k_a, for the solar radiation, used in the author's experiment, after passing through the borosilicate glass of the flask, was estimated to be approximately 0.3×10^{-4} per sec. This compares with the value of 2.7×10^{-4} per sec., calculated for the UV light normally used. It must also be remembered that the value of 2.7×10^{-4} per sec. is an average, as the calculated value of k_a for the UV light, varied from point to point inside the flask, in the range $.9 \times 10^{-4}$ per sec. to 7.3×10^{-4} per sec., approximately, due to the lack of uniformity in the intensity of the UV light, in this case.

It seems, that the specific absorption rate of sulphur dioxide for the natural sunshine, after transmission through the borosilicate glass, was not sufficiently high to cause UV nucleus formation, under the author's experimental conditions. It must be remembered however, that the specific absorption rate of sulphur

dioxide, for radiation from the sun at a zenith angle of 40°, would be much higher than 0.3×10^{-4} per sec. in the open atmosphere, since the radiation would not have to pass through the borosilicate glass, and the sky radiation would also be available. Leighton[6] gives the value of k_a to be 1.7×10^{-4} per sec., for direct and sky radiation from the sun in a clear sky, at a zenith angle of 40°.

Therefore just because natural sunshine, after passing through the borosilicate glass of the flask, failed to form UV nuclei, under the experimental conditions used, one cannot assume that such nuclei would not be produced by solar radiation in the open atmosphere, in heavily polluted air. As has been already mentioned in this work, there is strong evidence that nuclei are in fact formed by natural sunshine in polluted air.

AN ATTEMPTED ROUGH CHEMICAL ANALYSIS OF THE UV NUCLEI

An attempt was made to collect a sample of the UV nuclei on a Millipore filter, in order to analyse them, chemically. It has been shown in a previous experiment, that a Millipore filter of pore size 1.2 micron captures all UV nuclei in the air passing through it, at an airflow rate of 3.0 litres per minute. A white Millipore filter of pore size 1.2 micron mounted in a stainless steel holder, was placed in the airline between the flask and the pump. The dynamic experiment was carried out, at an airflow rate of 3 litres per minute, using outdoor air which had been filtered through cotton wool. The experiment was continued for a period of 10 days, so that most of the nuclei produced in the air in the flask by the UV radiation should have been deposited on the Millipore filter. However, at the end of this 10 day period there was no trace whatever of any visible deposit on the filter surface,

even on investigation under a microscope at magnifications up to 500. Since it was thought that the lack of a visible deposit might be due to the fact that the deposit was white and therefore of the same colour as the filter, the above experiment was repeated, using a black filter, but still, no deposit was detected. It may be, that the amount of matter in the nuclei collected over the period of 10 days was too small to be detected. This however, seems unlikely, as the author[26] was able to collect in a few days, on a similar filter, a very noticable dark brown deposit of nuclei produced by a heated platinum wire, at concentrations which were of the same order of magnitude as those for the UV nuclei, using a similar technique.

A sensitive chemical test for sulfates, was carried out on the surface of the filter which had been used to "collect" nuclei for 10 days. In this test, which was taken from the Millipore manual on microchemical and instrumental analysis[75], a reagent consisting of a saturated aqueous solution of lead nitrate, containing 1 c.c. of concentrated nitric acid per 25 c.c. of solution, was placed on a filter paper and the Millipore filter was placed on top of it, so that it soaked up the reagent. The presence of sulfate on the filter surface would have been indicated by the formation of white grainy reaction spots on the filter surface, visible under a microscope, with low magnification. The test was negative.

When the Millipore filter was wetted, after the experiment, a red or blue litmus paper placed in contact with it showed no significant colour change. If there had been a sufficient number

of sulphuric acid nuclei on the filter surface, it would cause blue litmus to turn red.

The filter surface was also tested for the presence of hydrogen peroxide, since a number of workers have suggested that UV nuclei consist of hydrogen peroxide. The reagent used was a solution of benzidine in ethyl alcohol with added peroxidase. This solution changes colour from brown to a dark blue, when hydrogen peroxide is added. A drop of the reagent was placed on a piece of the Millipore filter used to "collect" the UV nuclei, but the test, which is very sensitive, was negative.

The results of this experiment suggest that the UV nuclei are not indefinitely retained on the filter, but that they are returned to the gaseous phase due to dissociation or chemical reaction, on the filter surface, or by evaporation into the air streaming through the filter.

THE EFFECT OF ADDING HYDROGEN TO THE AIR IN THE FLASK, ON UV NUCLEUS FORMATION

Hoppe[31] found that UV nucleus production in nitrogen was reduced by 30°/o, 60°/o and 90°/o when 2.10^{-3} °/o hydrogen, 8.10^{-3} °/o hydrogen and 2.10^{-2} °/o hydrogen respectively was added to the nitrogen. Nucleus production ceased altogether when 0.1°/o hydrogen was added.

It was decided to add hydrogen to the air in the flask, to see whether it would suppress UV nucleus formation, under the author's experimental conditions.

Experimental Procedure: The dynamic experiment was carried out

at an airflow rate of 1 litre per minute, using outdoor air which had been filtered through a Millipore filter. An arrangement was made to allow some hydrogen into the air, before it was filtered, and passed through the flask. The hydrogen could be released at a specified rate from a cylinder with a pressure reduction and regulating head, and added through a rotameter and a Y tubing, to the main airflow.

Three measurements of steady state UV nucleus concentration were made, just before hydrogen was added to the air. The mean of these three measurements was 2,930 per c.c. Hydrogen was now added at a rate of about 0.1 litre per minute, to the air passing through the flask. UV nucleus concentration fell to zero, in 22 minutes after the addition of hydrogen was commenced. After some time, the addition of hydrogen to the air passing through the flask, was stopped and nucleus concentration immediately began to increase, reaching a value of 2760 per c.c., 38 minutes later.

A similar experiment, was carried out, using outdoor air which had been filtered through cotton wool. In this case steady state UV nucleus concentration decreased from a mean value of 134,000 per c.c., to a mean value of 11,600 per c.c., 35 minutes after starting to add hydrogen, at the rate of 0.1 litre per minute. Nucleus production in this case did not drop to zero. When the addition of hydrogen was stopped, UV nucleus concentration increased again, reaching a value of 103,000 per c.c., 38 minutes later.

It seems therefore that the addition of approximately 10% hydrogen, by volume, caused a very large decrease in UV nucleus

formation, when the rate of nucleus formation was very high, and caused UV nucleus production, when relatively low, initially, to cease altogether.

Discussion of results:

Hoppe[31] explained the effect of hydrogen, on UV nucleus formation, as follows. He suggested that the UV nuclei were produced by a photochemical oxidation reaction, involving a trace gas such as sulphur dioxide, and atomic oxygen, which would be produced by the dissociation of molecular oxygen, which occurs photochemically, at wavelengths below about 2,400A, which Hoppe was using. The effect of hydrogen in this case, would be to bind the atomic oxygen so that it would not be available for the nucleus forming photochemical reaction. Hoppe, also found that when he added very small amounts of ammonia to UV irradiated atmospheric air, that UV nucleus production was suppressed. For this suppression, he blamed the atomic hydrogen assumed to be liberated in the photochemical dissociation of ammonia, according to the equation

$$NH_3 + h\nu \rightarrow NH_2 + H \qquad (1)$$

which occurs at wavelengths below, about 2300A. He found that the ammonia did not interfere with the growth of the nuclei, once they were formed, that its suppressing influence occurred earlier in the process of nucleus formation. The addition of larger amounts of ammonia led to an increase in nucleus production, probably due to a separate nucleus forming mechanism, involving the ammonia.

The author's results suggest that hydrogen interferes in the

process of UV nucleus formation, in city air with UV light of wavelength greater than 2900A. In the author's experiments, it is possible, but unlikely, that atomic oxygen is involved in the process of nucleus formation. The wavelengths of light used are much higher than 2400A, the wavelength below which dissociation of molecular oxygen occurs. According to Leighton[6], only two processes in polluted atmospheric air are known to lead to the formation of atomic oxygen. These processes are, the primary photochemical dissociation of ozone and of nitrogen dioxide. The concentration of atomic oxygen in city air is extremely low, and is believed to be smaller than 1×10^{-6} pphm.

The author found very strong evidence that sulphur dioxide is involved in the process of UV nucleus formation in city air. Hydrogen may interfere in the process of nucleus formation, by reacting with excited sulphur dioxide molecules, according to the equation

$$SO_2' + 3H_2 \rightarrow 2\,H_2O + H_2S \qquad (2)$$

According to Mellor[76], unexcited sulphur dioxide does not take part in this reaction, at room temperature, with both gases dry, but the reaction occurs at temperatures above 280°C.

THE EFFECT OF RUBBER CONNECTING TUBING IN THE APPARATUS, ON UV NUCLEUS FORMATION

Atkinson[20] found that the UV nucleus forming power of air stored in a conventional cloud chamber with a rubber diaphragm, increased with the time of storage of the air in the cloud chamber. He claimed that at least a major part of the nuclei were produced from some contamination emitted by the rubber. Atkinson used light of wavelength much lower than the wavelengths of the UV light used in the author's experiments.

The rubber connecting tubing in the author's apparatus is not thought to have affected UV nucleus formation significantly. The rubber itself was at no stage exposed to the UV radiation. When air was stored in the flask, with some rubber in the flask, UV nucleus production in the air did not increase with storage time, but decreased, instead. UV nuclei were produced, as usual in the air in the flask, when no rubber was in contact with the air, during irradiation. The production or lack of production of UV nuclei in the air in the flask, depended on the treatment of the air used, and not on the presence or absence of rubber. It seems that UV nuclei were not formed by a reaction between sulfhur dioxide and any emanation from the rubber, since there was no nucleus production, when a low concentration of sulphur dioxide in a mixture of nitrogen and oxygen was irradiated.

THE CHEMISTRY OF UV NUCLEUS FORMATION

The aim of this chapter is to discuss the chemical reactions which are most likely to lead to UV nucleus formation in city

air, using UV radiation of wavelength greater than 2900A. Wavelengths lower than 2900A have not been detected in solar radiation, in the lower atmosphere.

It is assumed that the UV nuclei are formed as a result of a photochemical reaction involving at least one trace gas present in Edinburgh air. This trace gas, since it takes part in such a reaction, must absorb some of the UV light present in solar radiation. The most important gases or vapours, likely to be present in polluted air, and which absorb UV radiation in the region 3000A to 7000A, are, according to Leighton[6]: ozone, nitrogen dioxide, sulphur dioxide, nitric acid and alkyl nitrates, nitrous acid and alkyl nitrites and nitro compounds, aldehydes, ketones, peroxides, acyl nitrites and pernitrites and nitrates. The most important gases or vapours, likely to be present in city air, which do not absorb solar radiation are as listed by Leighton: nitrogen, water, carbon monoxide, carbon dioxide, nitric oxide, sulphur trioxide, sulphuric acid, hydrocarbons, alcohols and organic acids.

It is likely that the trace gas or vapour which takes part in the photochemical reaction, leading to UV nucleus formation, is listed among the absorbing gases and vapours above. The results of the author's experiments have afforded very strong evidence that sulphur dioxide takes part in the photochemical reaction leading to UV nucleus formation.

The Nature of a Photochemical Reaction: The first step in a photochemical reaction is the absorption of radiation. According to the Stark-Einstein law of photochemical equivalence, one molecule of absorbent absorbs one photon, so that the number of

molecules absorbing, is equal to the number of photons absorbed. The process of absorption by a molecule X of absorbent, can be expressed by the equation

$$X + h\nu \rightarrow X' \qquad (1)$$

where $h\nu$ is the energy of the absorbed photon, h and ν being Planck's constant, and the frequency of the light absorbed, respectively. The absorbing molecule is in an excited state, expressed as X', immediately after absorption, its extra energy above it's normal energy state being equal to the energy $h\nu$ of the photon which it absorbed. It seems that light which produces only vibrational or rotational changes in the absorbing molecule is photochemically inactive, and it is only when the light absorbed results in an electronic transition, leaving the absorbing molecule electronically excited, that sufficiently large changes are produced to lead to a chemical reaction.

After absorption of a photon, the electronically excited molecule X' may undergo any of several fates.

(a) It may internally rearrange or polymerize.

(b) It may lose its excitation energy by fluorescence;

$$X' \rightarrow X + h\nu \qquad (2)$$

(c) It may lose its excitation energy by collisional deactivation;

$$X' + M \rightarrow X + M \qquad (3)$$

M is any other molecule.

(d) It may dissociate;

$$X' \rightarrow x_1 + x_2 + \ldots. \qquad (4)$$

x_1, x_2 etc. are dissociation products.

(e) It may react with another molecule A on collision;

$$X' + A \rightarrow B_1 + ... \qquad (5)$$

B_1 etc. are photochemical reaction products.

Only the two processes (d) and (e) lead to a photochemical change. The processes (b) and (c) merely return the absorbing molecule to its normal state.

A primary photochemical reaction is defined as the first chemical reaction after the absorption of a photon by the molecule. The reaction products of a primary photochemical reaction may take part in secondary photochemical reactions.

The quantum yield $\emptyset$: The quantum yield $\emptyset$, for a primary photochemical reaction, is the fraction of excited molecules which take part in that reaction.

The likely role of sulphur dioxide in the photochemical reaction leading to UV nucleus formation in city air:

The author's work has afforded convincing evidence that sulphur dioxide is involved in a primary or secondary photochemical reaction, leading to UV nucleus formation. The identity of the reaction partner of the sulphur dioxide is, however, very much in the dark. A number of possible reaction products will now be examined.

(1) Oxygen:

The most popularly quoted photochemical reaction involving sulphur dioxide, which is likely to lead to UV nucleus formation, is the photooxidation of sulphur dioxide to sulphur trioxide, with

subsequent formation with water vapour, of sulphuric acid droplets. Leighton[6], and Dunham[30], have discussed this reaction in detail. According to Leighton, the only observed reaction product of the photolysis of sulphur dioxide in the presence of air or oxygen, is sulphur trioxide, or if water is present, sulphuric acid. Gerhard and Johnstone[77], using 5-30 ppm. of sulphur dioxide in moist air, exposed to a mercury sunlamp, found that the rate of sulphuric acid formation was directly proportional to the sulphur dioxide concentration.

The rate of the photooxidation of sulphur dioxide: The photolysis rate constant k, for the photooxidation of sulphur dioxide to sulphur trioxide is defined as the fraction of sulphur dioxide molecules converted to sulphur trioxide molecules, per unit time. The value of k is given by the equation,

$$k = \phi k_a \qquad (6)$$

where k_a is the specific absorption rate of sulphur dioxide for the UV radiation used, and ϕ is the quantum yield, for the photooxidation reaction. The approximate value of k_a, has already been calculated in this work, for the UV light irradiating the air in the flask, under the author's standard experimental conditions, and found to be, 2.7×10^{-4} per sec. Values of k_a have also been given for natural sunshine, from a clear sky, for various solar zenith angles. Leighton[6] gives values of the quantum yield ϕ, calculated from observations on the photolysis rate constant k, made by various workers. These values of ϕ range from 3×10^{-3} to 3×10^{-1}, thus covering a range of about two orders of magnitude. The

reasons for such a large variation are not apparent.

The value of k, the photolysis rate constant for the photooxidation of sulphur dioxide to sulphur trioxide, for the author's experimental conditions, was calculated, using equation (6), and the above values of k_a and $\emptyset$, and was found to lie in the range 8.1×10^{-7} per sec. to 8.1×10^{-5} per sec.

The Mechanism of the Photooxidation of sulphur dioxide:

The mechanism of the photooxidation of sulphur dioxide to sulphur trioxide is obscure.

It has been already noted in this work that the energy of a photon of UV light of wavelength greater than 2900A, is not sufficient to cause dissociation of a sulphur dioxide molecule. Therefore, the primary photochemical processes following absorption of UV light of wavelength greater than 2900A, must involve excited sulphur dioxide molecules.

The following primary processes involving excited sulphur dioxide molecules, based on postulations by Hall[52], Blacet[78], and Dainton and Ivin[32], may take place.

$$SO_2 + h\nu \rightarrow SO_2' \qquad (7)$$

$$SO_2' \rightarrow SO_2'' \qquad (8)$$

$$SO_2'' + M \rightarrow SO_2 \qquad (9)$$

$$SO_2' + SO_2 \rightarrow SO_2 + SO_2 \qquad (10)$$

$$SO_2' + N_2 \rightarrow SO_2 + N_2 \qquad (11)$$

$$SO_2' + O_2 \rightarrow SO_2 + O_2 \qquad (12)$$

$$SO_2' + O_2 \rightarrow SO_4 \qquad (13)$$

Process (7) merely shows that absorption of a photon by the sulphur dioxide molecule produces an excited sulphur dioxide molecule. Dainton and Ivin[32] postulated that the excited state SO_2' might be a triplet, which may degrade by internal transfer, to a vibrationally excited ground state, SO_2'', which is subsequently deactivated by collision with any molecule M (processes (8) and (9)). It must be assumed that the initial excited state SO_2' is deactivated only by this interal rearrangement, or by collision, since fluorescence of sulphur dioxide has not been observed at wavelengthsabove 2100A.

Processes (10), (11) and (12) are collisional deactivations, by molecules of sulphur dioxide, nitrogen, and osygen respectively. Dainton and Ivin obtained evidence that the efficiency of sulphur dioxide and nitrogen, as the deactivating species in processes (10) and (11), is small. Anyway, the importance of process (10) would be negligible, under the author's experimental conditions, as the sulphur dioxide concentration was very low.

Secondary reactions of SO_4, which might lead to the formation of sulphur trioxide or sulphuric acid are;

$$SO_4 + SO_2 \rightarrow 2\,SO_3 \qquad (14)$$

$$SO_4 + O_2 \rightarrow SO_3 + O_3 \qquad (15)$$

$$SO_2 + O_3 \rightarrow SO_3 + O_2 \qquad (16)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (17)$$

At the low sulphur dioxide concentrations in city air, reaction (14) should be of minor importance. Reaction (16) has been shown by Blacet[78], Gerhard and Johnstone[77], and Dunham[30] to be of minor importance. Their results indicated that oxidation of the sulphur dioxide by ozone was insignificant compared to the action initiated by the absorption of radiation by the sulphur dioxide molecule.

Cadle[85], quotes the following process,

$$2\ SO_2 + O_2 + h\nu \rightarrow 2\ SO_3 \qquad (18)$$

as the photochemical reaction causing photooxidation of sulphur dioxide, in sunlight.

Calculation of the rate of formation of sulphur trioxide molecules

It is assumed in the following calculations that the sulphur dioxide concentration in the air is 10 pphm., which is of the correct order of magnitude for moderately polluted city air. This concentration is equivalent to a concentration of molecules of sulphur dioxide, of 2.46×10^{12} molecules per c.c. at a temperature of 25°C, and at a pressure of 760 mm. Hg. The number of molecules of sulphur dioxide, receiving photons, per sec., under the author's experimental conditions, is therefore given by $2.46 \times 10^{12} \times k_a$, where k_a is the specific absorption rate of sulphur dioxide, for the UV radiation used. Since the value of k_a is 2.7×10^{-4} per sec., the number of molecules of sulphur dioxide receiving photons, per c.c. per sec., is calculated to be approximately 6.6×10^{8} molecules per c.c. per sec.

The residence time of the air in the flask, in a dynamic experiment carried out at an air flow rate of 1 litre per minute,

was 6.5 minutes. The fraction of molecules of sulphur dioxide, in the air, receiving photons in that time was calculated to be approximately 0.1. This means that a maximum of 0.1 of the sulphur dioxide, in the air in the flask, would be consumed during this 6.5 minutes. The actual fraction consumed in the photooxidation process would be $0.1 \times \emptyset$, where $\emptyset$ is the quantum yield, which, as mentioned already, seems to have a value between 3×10^{-3} and 3×10^{-1}. The above calculation suggests that the rate of consumption of sulphur dioxide, under the experimental conditions used by the author, should be very small. This calculation is in agreement with the results of an experiment carried out by the author, which was described on pages 63-65 of this work.

The number of molecules of sulphur dioxide per c.c., receiving photons, during the residence time of 6.5 minutes, is calculated to be approximately 2.6×10^{11} molecules per c.c., assuming an initial sulphur dioxide concentration of 10 pphm.

The calculated value of the photolysis rate constant k, for the photooxidation of sulphur dioxide to sulphur trioxide, for the author's experimental conditions, was found to lie in the range 8.1×10^{-7} per sec., to 8.1×10^{-5} per sec. Using these values, and the value of the sulphur dioxide molecular concentration, 2.46×10^{12} molecules/c.c., corresponding to 10 pphm., the number of molecules of sulphur trioxide, being formed per c.c. per sec., under the author's experimental conditions, was calculated to lie in the approximate range $2 \times 10^{6} - 2 \times 10^{8}$ molecules per c.c. per sec.

Similarly, the number of sulphur dioxide molecules per c.c.,

converted to sulphur trioxide, during the 6.5 minutes residence time of the air in the flask, in a dynamic experiment, at an airflow rate of 1 litre per minute, was calculated to be between 7.8×10^{8} and 7.8×10^{10} molecules per c.c.

Time needed to achieve saturation of the air with sulphuric acid, under the author's experimental conditions:

One of the more satisfactory mechanisms proposed for the formation of condensation nuclei from sulphuric acid molecules, produced as a result of the photooxidation of sulphur dioxide, has been the mechanism of nucleation due to chemical supersaturation of the air, with sulphuric acid molecules. This chemical supersaturation hypothesis has been discussed in various parts of this work. This hypothesis suggests that substantial nucleation, would occur when a certain critical supersaturation of the air with sulphuric acid molecules, was achieved. This critical supersaturation is probably of the order of ten-fold saturation.

It would be interesting to find out how long it would take to achieve saturation of the air with sulphuric acid molecules, with the rate of formation of sulphur trioxide molecules which has been calculated for the author's experimental conditions, and a sulphur dioxide concentration of 10 pphm. This calculation would enable one to find out approximately the theoretical "time delay" between the commencement of UV irradiation of the air and the onset of substantial nucleation.

The assumption is made, that each sulphur trioxide molecule photochemically produced, reacts with a water molecule to form a sulphuric acid molecule, according to reaction (17). This is a

reasonable assumption, since reaction (17) is very efficient, and the air always contains an ample concentration of water molecules.

The concentration of sulphuric acid molecules in the vapour of concentrated sulphuric acid, at equilibrium

The vapour of concentrated sulphuric acid consists of water molecules, and sulphuric acid molecules. The equilibrium vapour pressure of the sulphuric acid component of the vapour, over a plane surface of 90°/o sulphuric acid (in water), at a temperature of 25°C, was calculated, using values of the constants A and B of the Clapeyron-Clausius equation, given by Baranova[79]. The values of A and B respectively were 9.850 and 4525. The corresponding form of the Clapeyron-Clausius equation is,

$$\log_{10} P = A - \frac{B}{T} \qquad (19)$$

where P is the pressure of the saturated vapour, in mm. of Hg, at the absolute temperature T. The equilibrium vapour pressure of the sulphuric acid component of the vapour, was calculated to be approximately 4.8×10^{-6} mm. Hg, at 25°C. This is equivalent to a density of sulphuric acid molecules, of approximately 1.5×10^{11} molecules per c.c.

Dunham[46], when calculating theoretical nucleation rates after chemical supersaturation of air by sulphuric acid, gave corresponding values of the maximum supersaturation reached, and the time taken to reach it, for two different steady rates of formation of sulphuric acid molecules. It seemed from these corresponding values, that Dunham used a value of about 4.8×10^{10} molecules per c.c., as the equilibrium concentration of sulphuric

acid molecules, over a plane surface of 100°/o sulphuric acid. The pressure of the sulphuric acid component of the vapour, over a solution of sulphuric acid in water, increases with the concentration of the sulphuric acid, whereas the pressure of the water vapour component decreases. Therefore, the value of 4.8×10^{10} molecules per c.c., for the equilibrium concentration of sulphuric acid molecules, over a plane surface of 100°/o sulphuric acid, which seems to have been used by Dunham, appears to be incompatible with the equilibrium concentration of 1.5×10^{11} molecules per c.c., over a plane surface of 90°/o sulphuric acid, which was calculated, using the constants given by Baranova.

The time needed to saturate the air with sulphuric acid molecules, was calculated, using the smaller value of 4.8×10^{10} molecules of sulphuric acid per c.c., as the concentration of sulphuric acid molecules in the vapour over a plane surface of 100°/o sulphuric acid, at saturation, and using the approximate rate of formation of sulphuric acid molecules, 2×10^{6} to 2×10^{8} molecules per c.c., which was calculated for the author's experimental conditions, and a sulphur dioxide concentration of 10 pphm. This time, needed to build up saturation, was calculated to lie between 4.0 and 40.0 minutes, approximately. Since substantial nucleation would not occur until a supersaturation of the order of ten-fold saturation had been achieved, there would be a "time delay" of the order of 40 to 400 minutes, between the commencement of irradiation of the air, and the beginning of such nucleation. This is much longer than the "time delay" of the order of one minute, observed in the author's experiments.

In the calculation of the above "time delay", it was assumed that the nuclei consist of 100°/o sulphuric acid. As is mentioned elsewhere in this work, (see page 96), it is unlikely that nuclei produced in the atmosphere, as a result of the photochemical formation of sulphuric acid, would consist of 100°/o sulphuric acid. These nuclei would be more likely to consist of sulphuric acid, diluted by water. The equilibrium concentration of molecules of sulphuric acid, over a plane surface of this dilute sulphuric acid, would decrease with the amount of dilution of the sulphuric acid, so that, with a particular dilution a "time delay" of the same order of magnitude as the "time delay" found in the author's experiments, would apply.

Leighton[45] states that the particulate formed from photooxidation of sulphur dioxide in air of 50°/o relative humidity, consists of droplets of about 43°/o sulphuric acid (in water). According to Brasted[80], "moisture" in the atmosphere and sulphur trioxide combine to form a rather inert fog. He stated that physicochemical methods of examination of this fog, over a wide range of temperatures (-23°C to 35°C) and over a wide range of concentrations, (0.62 to 99.85 mole °/o of sulphur trioxide), indicated that three distinct compounds existed, these being; $SO_3 \cdot H_2O$ (H_2SO_4) ; $SO_3 \cdot 2H_2O$($H_2SO_4 \cdot H_2O$); and $2\ SO_3 \cdot H_2O$ ($H_2S_2O_7$). It seems probable that under the author's experimental conditions, with the very low concentrations of sulphur trioxide assumed to be produced, and the relatively high concentration of water vapour, that by far the most likely of these compounds would be the $SO_3 \cdot 2\ H_2O$ ($H_2SO_4 \cdot H_2O$) which

has two sulphur trioxide molecules, and four water molecules. According to Newton Friend[81], there is much evidence that hydrates of sulphuric acid are formed, such as; $H_2SO_4.H_2O$; $H_2SO_4.2H_2O$; and $H_2SO_4.4H_2O$. If the UV nuclei consist of a compound such as $SO_3.2H_2O(H_2SO_4.H_2O)$, or $H_2SO_4.2H_2O$, this is equivalent to a composition of the nuclei, of moderately dilute sulphuric acid of approximately 50°/o strength. This compares with the approximate strength of 43°/o sulphuric acid quoted by Leighton, for the nuclei formed in air of 50°/o relative humidity.

Large "molecules" as nuclei: It is conceivable that large "molecules" of compounds such as $SO_3.2H_2O(H_2SO_4.H_2O)$ or $H_2SO_4.2H_2O$, could act as relatively insensitive nuclei, without any need for nucleation to be caused by chemical supersaturation. However this seems unlikely as such nuclei would contain too small an amount of hygroscopic material to make small drops formed on them stable against re-evaporation.

Is oxygen the reaction partner of sulphur dioxide, in the photochemical reaction leading to UV nucleus formation in city air?

Many workers have assumed that nuclei are formed as a result of the photooxidation of sulphur dioxide in air. The author's calculations have shown that sulphuric acid molecules ought to be produced at a sufficient rate, on UV irradiation of city air, to account for the concentration of nuclei produced, in his experiments. The results of most of the author's experiments are consistent with the above assumption. It seems from the results of one experiment, that it is necessary for UV

nucleus production, that water vapour is present in the air, on irradiation. Water vapour is needed to form sulphuric acid molecules from the sulphur trioxide molecules produced photochemically.

However the results of one series of experiments carried out by the author (see pages 152-162) were in serious disagreement with the assumption that the UV nuclei are formed as a result of the photooxidation of sulphur dioxide. It was found that no UV nuclei were produced when sulphur dioxide, was added to a pure mixture of 79°/o nitrogen and 21°/o oxygen (by volume), at a relative humidity of about 50°/o, at concentrations which were of the same order of magnitude as the sulphur dioxide concentrations found in Edinburgh air. However when sulphur dioxide was added, at similar concentrations, to relatively pure filtered atmospheric air, there was copious UV nucleus production, although this filtered atmospheric air, on its own, did not form any UV nuclei on irradiation. The results of this series of experiments, suggest that the photochemical reaction leading to UV nucleus formation, is a reaction between sulphur dioxide, and some other trace gas present in city air. This was also the conclusion reached by Aitken[11]. It is possible, however, that there is some substance present in city air, but absent in the cylinder nitrogen and oxygen used in the author's experiment, which acts as a catylist for one of the reactions leading to sulphuric acid formation, in the process of the photooxidation of sulphur dioxide.

Alternative reaction partners to oxygen, for sulphur dioxide, in the photochemical reaction leading to UV nucleus

formation will now be discussed. The first likely reaction partners discussed, are those that may take part in photochemical reactions with sulphur dioxide, resulting in the same reaction product, sulphuric acid, as the photochemical reaction of sulphur dioxide with oxygen.

(2) Ozone:

The reaction of sulphur dioxide with ozone,

$$SO_2 + O_3 \rightarrow SO_3 + O_2 \qquad (16)$$

has already been discussed, but is mentioned again, here, for the sake of completeness. Ozone is formed in the atmosphere by UV radiation and by electrical discharges. According to Haagen-Smit[5], concentrations of ozone of 50 pphm. have been repeatedly measured during heavy smogs in Los Angeles.

Experimental results obtained by Blacet[78], Gerhard and Johnstone[77], and Dunham[30], indicated that reaction (16) was of minor importance compared to the action initiated by the absorption of UV radiation by the sulphur dioxide molecule.

(3) Oxygen Atoms:

The secondary photochemical reaction of oxygen atoms with sulphur dioxide,

$$O + SO_2 + M \rightarrow SO_3 + M \qquad (20)$$

is quite fast, according to Kaufman[83]. M is any other molecule. Reaction (20) would be followed by the rapid reaction

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (17)$$

The only known reactions in the lower atmosphere, which lead to oxygen atom formation, are the primary photochemical dissociations of nitrogen dioxide and of ozone. According to Leighton[6], the maximum concentration of oxygen atoms in polluted air, is probably of the order of 3×10^{-6} pphm. The concentration of oxygen atoms produced in the air in the flask, in the author's experiment, would be of the same order of magnitude. The rate of formation of sulphur trioxide molecules, by reaction (20), was calculated, using a value of the concentration of 10 pphm. sulphur dioxide, and 3×10^{-6} pphm. oxygen atoms, and using the value of the rate constant for this reaction, obtained by Kaufman. The rate of formation of sulphur trioxide molecules, under these conditions was calculated to be approximately 3.4×10^{6} molecules per c.c. per sec. This compares with the value of approximately $2 \times 10^{6} - 2 \times 10^{8}$ molecules per c.c. per sec., calculated for the rate of formation of sulphur trioxide molecules by photooxidation of sulphur dioxide. It must be remembered that the oxygen atom concentration of 3×10^{-6} pphm. is an upper limit. Therefore it seems that reaction (20) is unimportant, compared to the photooxidation of sulphur dioxide, unless the value of the quantum yield for the photooxidation of sulphur dioxide is in lower region of the estimated range of 3×10^{-3} to 3×10^{-1}.

(4) Hydrogen peroxide:

Hydrogen peroxide is formed in the lower atmosphere, probably according to the following secondary photochemical reaction, given by Mason[44]

$$H_2O + O_3 \rightarrow H_2O_2 + O_2 \qquad (21)$$

Sulphuric acid would then be formed, according to the reaction,

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \qquad (22)$$

It is doubtful however, if sufficient hydrogen peroxide would be produced on irradiation of atmospheric air, under the author's experimental conditions, to make reaction (22) significant.

(5) Ammonia:

According to Junge[82], the predominant part of the soluble material of atmospheric condensation nuclei, in the radius range 0.08 to 0.8 micron, consists of NH_4 and SO_4. No exceptions from this rule were found in measurements made in Frankfurt, Germany; Round Hill, Mass., U.S.A.; Florida, U.S.A. , and Hawaii. The ratio of NH_4 to SO_4 indicated that these substances were present as a mixture of $(NH_4)_2\ SO_4$ and $(NH_4)\ HSO_4$. The highest concentration of both NH_4 and SO_4 were found in densely populated areas, so that their formation as a result of human activity seems obvious. According to Junge, there is strong evidence that the ammonium sulphate in the nuclei is formed by a gas reaction between ammonia and sulphur dioxide. He stated that experimental investigations show that this reaction occurs with very small concentrations, and that field measurements indicated that ammonia and sulphur dioxide are always present in the atmosphere in amounts large enough to account for the ammonium sulphate in the aerosols.

It seems likely that ammonium sulphate or ammonium hydrogen sulphate, would be formed by a reaction between sulphuric acid, photochemically formed from sulphur dioxide, according to one of

the processes already described in this chapter, and ammonia, according to the reactions;

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2\ SO_4 \qquad (23)$$

$$NH_3 + H_2SO_4 \rightarrow (NH_4)\ HSO_4 \qquad (24)$$

Aitken[11] found that ammonia and sulphur dioxide reacted in the dark, and did not need light energy. He concluded therefore that ammonia was not the reaction partner for sulphur dioxide, in the photochemical reaction leading to nucleus formation.

Hoppe[31] found that when he added amounts of ammonia less than about 1 mm. Hg, to atmospheric air, that UV nucleus formation was suppressed (see page 184). For this suppression, he blamed the atomic hydrogen assumed to be liberated in the photochemical dissociation of ammonia, which occurs at wavelengths below 2300A. Since wavelengths shorter than 2900A were not present in the UV light used by the author, and are not present in natural sunshine, ammonia would not be expected to have the same suppressing influence on the production of nuclei by these radiations.

According to Mason[44], ammonia in the atmosphere results from combustion processes and from decomposition of organic (particularly animal) matter.

(6) Hydrocarbons:

Dainton and Ivin[32] reported an aerosol forming photochemical reaction between sulphur dioxide and hydrocarbons, both olefins and paraffins. Analysis of the collected aerosol,

an involatile colourless or pale yellow oil with a disagreeable odor, suggested that it was a sulfinic acid, with some disulfinic acid.

However, it seems that Dainton and Ivin used light of wavelength much lower than 2900A. The effect of oxygen on the reaction or on aerosol formation was not investigated. The concentrations of sulphur dioxide and hydrocarbons used, were much higher than the concentrations found in heavily polluted city air. According to Leighton[6], the quantum yield of the sulphur dioxide-hydrocarbon reaction, at the hydrocarbon concentrations found in city air, would probably be extremely small, perhaps of the order of 10^{-6}. This reaction may, therefore not be significant in the open atmosphere, or under the author's experimental conditions.

(7) Hydrocarbons and oxides of nitrogen:

Schuck, Ford and Stephens[33] found dramatic increases in the rate of aerosol formation by irradiation of motor car exhaust-air mixtures, when sulphur dioxide was added to the gas mixtures. Schuck and Doyle[34], and Renzetti and Doyle[35], reported a similar effect, when sulphur dioxide was added to nitrogen oxide-nitrogen dioxide-hydrocarbon mixtures in air. The chemical nature of the particulate formation in the UV irradiation of sulphur dioxide-nitrogen oxides-hydrocarbon mixtures, has not been determined. Analysis of the aerosol formed by irradiation of dilute motor car exhaust in air, showed that the amount of aerosol produced was a function of the sulphur content of the fuel, and that the aerosol had a very high organic content, in excess of 66°/o, with about

8.4°/o SO_4 and 10.3°/o NO_3 for a particular fuel, (Schuck, Ford and Stephens[33]). However, this finding throws no light on the initial reaction causing the nucleus formation, as chemicals other than those directly involved in the nucleus formation are probably absorbed or condensed on the initial particle, masking its identity.

Doyle[34,35] carried out experiments on the particulate formation by photolysis of mixtures of sulphur dioxide, nitrogen oxide and an olefin hydrocarbon, in air. In one experiment, the light scattering, referred to air, from the aerosol formed, due to UV irradiation of 0.1 ppm. sulphur dioxide, in air, was 0.75. With 1 ppm. nitrogen oxide and 3 ppm. of 2-methyl-2-butune, in air, the light scattering was 0.4. With a mixture of 0.1 ppm. sulphur dioxide, 1 ppm. nitrogen oxide, and 3 ppm. 2-methyl-2-butene, the light scattering referred to air was 8.5, that is 11 times greater than the light scattering from the aerosol formed with 0.1 ppm. sulphur dioxide, only.

Doyle irradiated mixtures of 0.1 - 0.6 ppm. sulphur dioxide, 1 ppm. nitrogen oxide, and 3 ppm. of various hydrocarbons. He found that when paraffins were used, no observable light scattering aerosol was produced, whereas when olefins were used, there was always production of light scattering aerosol.

Stevenson, Sanderson and Altshuller[84], showed that addition of sulphur dioxide to nitrogen dioxide-hydrocarbon-air mixtures, caused a large increase in the number of nuclei formed, on UV irradiation. They did not try sulphur dioxide alone, in air.

It seems therefore that the reaction partner of sulphur dioxide in the photochemical reaction leading to UV nucleus

formation, in the author's experiments, and in the open atmosphere, may be nitrogen oxides and hydrocarbons, particularly olefin hydrocarbons. These hydrocarbons are mainly liberated into the atmosphere from motor-car exhausts and crankcases.

Some of the sulphur dioxide-nitrogen oxides-olefin reactions are very fast, perhaps more than ten times as fast as the photo-oxidation of sulphur dioxide. The role of sulphur dioxide in the photochemical production of nuclei in polluted air has been questioned, due to the observed relatively low sulphur dioxide content of the air in the Los Angeles basin, which is notorious for photochemical smog. However, when sulphur dioxide is taking part in fast aerosol forming reactions, such as the sulphur dioxide-nitrogen oxides-olefin reaction, then the sulphur dioxide will be quickly consumed after liberation into the atmosphere, and little sulphur dioxide will remain free in the atmosphere, to be measured.

On the other hand, there is evidence that UV nuclei are produced in polluted air when there is an apparently negligible concentration of hydrocarbons present. Thus, Aitken[11], found that large numbers of nuclei were produced by sunshine in the air in Falkirk, central Scotland, in the first decade of the 20th century, when there were very few motor cars liberating hydrocarbons into the atmosphere. Hydrocarbons of many kinds are liberated into the atmosphere naturally, in swamps and marshes.

(8) Other Organic Substances:

According to Went[4], considerable amounts of volatile organic substances are emitted into the air by many kinds of vegetation, in sunlight. A pine forest produces quantities

of volatile terpenes such as pinene, whereas the fragrance of meadows, sagebrush, and decaying leaves are due to volatile organic substances. Blue hazes produced over such vegetation in sunlight, when the wind velocity is low, probably consist of nuclei produced photochemically from these organic substances. O'Connor[36] and the author[26] have described the production of UV nuclei by UV irradiation of an emanation from decaying seaweed (fucus), in air.

It is possible that UV nuclei may be produced in atmospheric air as a result of a photochemical reaction between sulphur dioxide and some of these organic substances emitted by living and decaying vegetation.

(9) Chlorine:

Some free chlorine exists in the atmosphere, most probably liberated from the sodium chloride in large nuclei, or in droplets in the air, by some chemical reaction, possibly involving nitrogen dioxide (Cadle[85]. This reaction may be photochemical in nature.

Sulphur dioxide and chlorine react photochemically, in sunlight, as follows;

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2 \qquad (25)$$

The product of this reaction is sulphuryl chloride, a volatile fuming liquid, in bulk form, at room temperature. It is doubtful if there is sufficient free chlorine in the atmosphere to make this reaction significant. Anyway, since sulphuryl chloride is volatile, it would not form stable condensation nuclei, on its own.

Conclusion:

It seems that the photochemical reactions of sulphur dioxide

with oxygen atoms, and with atmospheric oxygen (if this reaction is catylised by some substance in atmospheric air), may produce sufficient sulphuric acid molecules, to cause the production of nuclei consisting of moderately dilute sulphuric acid, by the mechanism of chemical supersaturation. There is evidence that the nuclei may be produced by a reaction between molecules of sulphuric acid produced by one of the above reactions, and ammonia in the atmosphere. The only other likely nucleus forming reaction is the sulphur dioxide-nitrogen oxides-olefin reactions. It seems that the photochemical reaction leading to UV nucleus formation, only proceeds in the presence of water vapour.

CONCLUSIONS

Very strong evidence has been found that the formation of uncharged condensation nuclei in filtered Edinburgh air, by UV radiation of wavelength greater than 2900A, was due to a photochemical reaction involving sulphur dioxide. The intensity of the UV light used, weighted according to absorption by sulphur dioxide, was calculated to be approximately equal to the similarly weighted intensity of the direct and indirect radiation from the sun, at the zenith in a clear sky.

It seems that these UV nuclei are only formed when water vapour is present in the air, on irradiation. The nuclei may be produced from sulphuric acid molecules formed by water vapour and sulphur trioxide. The sulphur trioxide would result from the catylised photochemical reaction of sulphur dioxide and molecular oxygen or from the reaction of sulphur dioxide with atomic oxygen, formed by the photochemical dissociation of nitrogen dioxide and ozone. Alternatively the nuclei may be formed from ammonium sulphate or ammonium hydrogen sulphate, which would be produced by a reaction of sulphuric acid molecules produced as above, and ammonia. Another possible reaction leading to UV nucleus formation, is the photochemical reaction of sulphur dioxide with a mixture of nitrogen oxides and olefin hydrocarbons.

The nuclei are probably formed, due to a chemical supersaturation of the air with the material of the nuclei.

Importance of UV nuclei in the atmosphere:

It is probable that UV nuclei similar to those observed in the author's experiments, are produced in the open atmosphere, when both the pollution level of the air, and the intensity of solar radiation, weighted according to absorption by sulphur dioxide, are sufficiently high. It must be remembered, however, that the concentration of UV nuclei produced in untreated atmospheric air would be smaller than the concentration produced in filtered atmospheric air. This would be so, because the nucleogenic material, photochemically produced, would partly condense on nuclei already existing in untreated atmospheric air, rather than form new nuclei (see pages 84-87).

The layer of relatively large sulphate particles found at a height of 20 km. in the stratosphere, and described by Junge et al[86,87] and Byers[88], almost certainly owe their formation to a photochemical reaction involving sulphur dioxide. It is also possible that the particles, which act as nuclei for the ice crystals believed by some workers such as Paton[89] to form noctilucent clouds, may have a photochemical origin.

Photochemical "smog" or haze formation is a serious problem in numerous cities, such as Los Angeles. When such a "smog" or haze is formed, the haze particles or nuclei act as centres of physical or chemical condensation for various pollutants. Since large concentrations of various pollutants are then present in the nuclei, reactions can occur in the nucleus or on the nucleus surface, which would not take place in the absence of haze. Photochemical haze is injurious to health, causing irritation of the eyes and of the respiratory tract. It should

be realised that for proper control of air pollution, it is not sufficient to control emission into the atmosphere of visible smoke only, but that the emission of trace gases and vapours, particularly sulphur dioxide, should also be controlled.

Possible use of condensation nuclei techniques, for the chemical analysis of trace gases

The formation of UV nuclei in filtered atmospheric air was found to increase with the sulphur dioxide concentration. It seems therefore, that a method could be developed to measure the concentration of sulphur dioxide in the atmosphere or in a gas mixture, by forming nuclei from sulphur dioxide and its reaction partner using UV radiation, under carefully controlled conditions. The concentration of nuclei produced would be measured by means of a suitable nucleus counter. Similar methods could be used for the chemical analysis of other trace gases such as ammonia, hydrogen sulphide, and hydrocarbons, which are known to take part in photochemical reactions leading to UV nucleus formation. However, it is stressed that since there is very little information available, on the production of UV nuclei by irradiation of various gases and vapours, that there is need for much more research on this problem, before the above method will be of practical use.

Suggestions for future research:

It is extremely important that great care should be taken in future experiments on the production of nuclei by UV irradiation to use experimental conditions similar to the conditions obtaining in the atmosphere, if it is desired to use the results

of such experiments to find out what may happen in the open atmosphere. Thus the UV radiation used, should not contain light of wavelengths lower than the wavelengths of sunlight in the lower atmosphere. The intensity of the UV light used should be as uniform as possible and of the same order of magnitude as the intensity of sunlight in the lower atmosphere. The concentrations of trace gases and vapours used in such experiments should be of the same order of magnitude as the concentrations found in the atmosphere. Great care should be taken that no materials are used in the apparatus, especially in the irradiation chamber, which might form nuclei on irradiation.

It should be extremely interesting to investigate in detail possible nucleus forming photochemical reactions between sulphur dioxide and the various reaction partners discussed in chapter 27, particularly the reactions of sulphur dioxide with molecular oxygen, atomic oxygen, ammonia, and a mixture of nitrogen oxides and olefin hydrocarbons. It is stressed again, that these investigations should be carried out under conditions similar to those obtaining in the atmosphere.

It is intended to continue the research reported in this work, along these lines.

APPENDIX I

THE NUCLEI PRODUCED BY A PERISTALTIC PUMP

A brief investigation of the nuclei produced by a peristaltic pump (see page 67), was carried out. This pump grips flexible tubing, normally of silicone rubber, between a fixed plate, and a rotating divided drum. This rotating divided drum, pushes little parcels of air along the tubing, providing a flow of air in the tubing. The rate of airflow through the tubing is controlled by regulating the speed of rotation of the drum.

Experimental Procedure:

In this investigation, the peristaltic pump was used to draw air directly through a 1.2 micron pore size Millipore filter and a rotameter. The tubing used at first, was silicone rubber tubing with $\frac{1}{16}$" walls and $\frac{3}{8}$" bore. The air was then passed directly into the nucleus counter, or into the counter bypass tube.

Results:

It was found that the nucleus concentration in the air, after passing through the pump, increased with the rate of airflow. Table 12, shows the average nucleus concentrations Z, corresponding to four airflow rates from approximately 0.5 litre per minute to 1.8 litre per minute, which was the maximum airflow rate that could be achieved with the peristaltic pump, using silicone rubber tubing.

TABLE (12)

Nucleus production by a Peristaltic pump.

airflow rate litres/min.	Z nuclei/c.c.
0.5	8,230
1.0	14,800
1.5	22,100
1.8	28,300

The nucleus concentration for a particular airflow rate was quite steady, varying by not more than $\pm$ 10°/o of the mean concentration.

When ordinary red rubber was used in the pump, instead of the silicone rubber tubing, the concentration of nuclei produced, using an airflow rate of 0.85 litre per minute, was too high to be measured by the photoelectric counter, at the standard overpressure of 160 mm. Hg, as the extinction of the counter light-beam, by the fog formed on the nuclei, was measured to be 100°/o. The measured extinction was still 100°/o for an overpressure of 100 mm. Hg, whereas for overpressures of 50mm. Hg and 30 mm. Hg, the extinctions were 98.2°/o and 88.5°/o respectively. An extremely high concentration of nuclei was therefore produced by the peristaltic pump, using red rubber tubing.

Effect of drying the air with silica gel:

It was thought that the nuclei might be produced by a homogeneous nucleation of water vapour, in the little parcels of air formed in the rubber tubing by the action of the pump. It was possible that these parcels of air might suffer a large adiabatic expansion at some stage of the pumping process, thus causing this homogeneous nucleation. If this mechanism were the correct one, no nuclei would be produced if the water vapour was removed from the air, before passing it through the pump. For this reason, the incoming air was now drawn through a silica gel drying tower, before drawing it through the Millipore filter and the pump. The nucleus concentration showed no drop, when this dried air was used, even 43 minutes after commencing to use the dry air. It seems therefore that the above mechanism is not responsible for the formation of the nuclei, and that the presence of water vapour is not essential for the nucleus formation.

An experiment investigating whether the peristaltic pump nuclei are electrically charged:

The following experiment was carried out, in order to find out whether the nuclei produced by the peristaltic pump were electrically charged. The cylindrical condenser already used in the experiment investigating whether the UV nuclei were charged, and described on page 120, was placed in the airline between the peristaltic pump and the counter. The mean of three measurements of nucleus concentration in the air which had passed through the condenser, with no voltage across the electrodes, was 8,360. The voltage across the condenser

electrodes was now switched to IKV. It was calculated that all nuclei of radii less than 3×10^{-5} cm., with at least, a single electronic charge, would be removed from the air, when the voltage across the condenser electrodes would be 145 volts. The rate of airflow used, was 0.5 litre per minute. The mean of three measurements of nucleus concentration, made with the voltage of IKV across the condenser electrodes, was 8,340. The voltage across the condenser electrodes was again switched to zero, and the mean of three more measurements of nucleus concentration was 7,980 per c.c. Ample time was allowed, after changing the voltage across the condenser, each time, for the condenser and the counter to be filled with a completely new sample of air, so that the nucleus concentration measured, corresponded to the new voltage.

Discussion of Results:

The results of this experiment suggest that the nuclei produced by the peristaltic pump are electrically uncharged. However, the build up of electrostatic charge on the inside of the rubber tubing, by the friction caused by the action of the pump, might be responsible for the formation of the nuclei. Nolan et al[90-93] observed that small uncharged nuclei were produced by an electrical discharge at a water surface, or at a metal point. Evans and Watson[28], and Watson[94], have described the production of nuclei by a high D.C. voltage applied to an electrode in a gas-vapour mixture.

The nucleus production could not be due to the heating of the rubber by the friction, due to the action of the pump, since it was observed that the nuclei appeared in the air

passing through the pump, immediately after switching on the pump, although it was some minutes before the rubber, at the point of maximum friction, became noticeably hot.

REFERENCES

(1) Aitken, John: Collected Scientific Papers of John Aitken, Cambridge University Press, (1923).

(2) Mason, B.J.: "Clouds, Rain and Rainmaking", Cambridge University Press, p. 19 (1962).

(3) Twomey, S.: "Measurements of Natural Cloud Nuclei," Journal de Recherches Atmospheriques, Vol. I, No. 3, pp. 101-105 (1963).

(4) Went, F.W.: "Blue Hazes in the Atmosphere," Nature, Vol. 187, No. 4738, pp. 641-643 (1960).

(5) Haagen-Smit: "The Control of Air Pollution," Scientific American, Vol. 210, No. I, (1964).

(6) Leighton, P.A.: "The Photochemistry of Air Pollution," Academic Press, New York and London (1961).

(7) Landsberg, H.: "Origin and Chemistry of Condensation Nuclei," Ergebnisse Der Kosmischen Physik, Leipzig

(8) Fletcher, N.H.: "The Physics of Rainclouds," Cambridge University Press, p. 65 (1962).

(9) Aitken, John: Trans. Roy. Soc. Edin., Vol. 39, No. I, p. 15 (1897)

(10) Aitken, John: "On Some Nuclei of Cloudy Condensation," Proc. Roy. Soc. Edin., Vol. 31, (1911), and: Collected Scientific Papers of John Aitken, Cambridge University Press, pp. 495-511 (1923).

(11) Aitken, John: "The Sun as a Fog Producer", Proc. Roy. Soc. Edin., Vol. 32, (1911-12) and: Collected Scientific Papers of John Aitken, Cambridge University Press, pp. 512-536 (1923).

(12) Verzár, F. and Evans, H.D.: "Production of Atmospheric Condensation Unclei by Sunrays", Geofisica Pura e Applicata, Milano, Vol. 43, No. 2, pp. 259-268 (1959).

(13) McLaughlin, P.J.: "Recherches sur les gros ions atmospheriques", La Meteorologie, Août (1928).

(14) Tyndall, : Phil. Trans., Vol. 160, P. 333 (1870).

(15) Lenard and Wolff; Wied. Ann., Vol. 37, p. 443 (1889).

REFERENCES (Contd.)

(16) Wilson, C.T.R.: "On the Condensation Nuclei produced in Gases by the action of Röntgen Rays, Uranium Rays, Ultraviolet Light, and other Agents", Phil. Trans. Roy. Soc. London, A192, 403-453 (1899).

(17) Saltmarsh, M.: "Experiments on Condensation Nuclei produced in Gases by Ultraviolet Light", Proc. Phys. Soc. London, Vol. 27 (1915).

(18) Crane, H.R. and Halpern, J.: Phys. Rev., Vol. 56, p.232 (1939).

(19) Farley, F.J.M.: Proc. Roy. Soc. A207, 527 (1951).

(20) Atkinson, J.R.: "Uncharged Condensation Nuclei produced ny Ultraviolet Light", Geofisica Pura e Applicata, Milano, Vol. 31, pp. 54-59 (1955).

(21) Evans, F.R: Personal communication.

(22) Barnard, A.J. and Mouton, W.L.: "Condensation Produced by Ultraviolet Light", Nature, Vol. 182, No. 4641, pp. 1001-1002 (1958).

(23) McHenry, J.J.: and Twomey, S: "Condensation Nuclei Produced by Ultraviolet Light", Proc. Roy. Irish Academy, Vol. 55, A, (1952).

(24) Verzár, F. and Kunz, V.: "Production of Atmospheric Condensation Nuclei by Solar Radiation", Geofisica Pura e Applicata, Milano, Vol. 38, pp. 215-221, (1957).

(25) McGreevy, G. and O'Connor, T.C.: "On the Production of Aitken Nuclei by Sunlight in St. Moritz", Geofisica e Meteorologica, Genoa, Vol. 10, No. 314 (1962).

(26) Roddy, A.F.: "The Production of Condensation Nuclei by Heated Wires and by Electromagnetic Radiation", M.Sc. Thesis, National University of Ireland, (1963).

(27) Vassails, G.: "Recherches sur les Gros Ions dans les Gaz", Annales de Physique, Vol. 12, No. 4, pp. 125-217 (1949).

(28) Evans, G.R. and Watson, A.A.: "Nitrogen Dioxide Vapour and the Creation of Condensation Nuclei," Proc. Roy. Soc., Edin., A, Vol. 67, No. 10, pp. 136-155 (1966).

(29) Mulcahy, M.T. and Kuffel, E.: "Condensation Nuclei produced by Ultraviolet Irradiation of Humid Air or Humid Argon", Proc. Phys. Soc., Vol. 80, pp. 1333-1342 (1962).

(30) Dunham, S.B.: "Detection of Photochemical Oxidation of Sulphur Dioxide by Condensation Nuclei Techniques", Nature, Vol. 188, No. 4744, pp. 51-52 (1960).

REFERENCES (Contd.)

(31) Hoppe, Walter: "Bildung von Kondensationskerner durch UV-strahlung in verschiedenen gasen", Geofisica Pura e Applicata, Geofisica Pura e Applicata, Vol. 50, No. 3, pp. 129-139 (1961).

(32) Dainton, F.S. and Ivin, K.J.: Trans. Faraday Soc., Vol. 46, p. 374, 382 (1950).

(33) Schuck, E.A., Ford, H.W. and Stephens, E.R.: "Air Pollution effects of Irradiated Auto exhaust as related to Fuel Composition", Air Pollution Foundation Report No. 26 (1958).

(34) Schuck, E.A. and Doyle, G.J.: "Photo-oxidation of Hydrocarbons in Mixtures containing Oxides of Nitrogen and Sulphur Dioxide", Report No. 29, Air Pollution, San Marino, California, (1959).

(35) Renzetti, N.A. and Doyle, G.J.: J. Air Pollution Control Assoc., Vol. 8, p. 293 (1959); International J. Air Pollution, Vol. 2, p. 327 (1960).

(36) O'Connor, T.C.: "On the Production of Condensation Nuclei by Gaseous Reactions", Journal de Recherches Atmospheriques, Vol. I, No. 3, pp. 127-133 (1963).

(37) Metnieks, A.L. and Pollak, L.W.: "Instruction for use of Photoelectric Condensation Nucleus Counters", Geophysical Bulletin No. 16, School of Cosmic Physics, Dublin Institute for Advanced Studies, (1959).

(38) Nolan, P.J. and Pollak, L.W.: "The Calibration of a Photoelectric Nucleus Counter," Proc. Roy. Irish Academy, A51, pp. 9-31,(1946).

(39) Aitken, John: "On a simple pocket dust-counter", Proc. Roy. Soc. Edin., Vol. 18, (1890-91) and "Collected Scientific Papers of John Aitken", Cambridge University Press, pp. 236-246 (1923).

(40) Pollak, L.W. and Metneiks, A.L.: "New calibration of photoelectric nucleus counters", Geofisica Pura e Applicata, Milano, Vol. 43, pp. 285-301, (1959).

(41) Pollak, L.W. and Daly, J.: "An improved model of the condensation nucleus counter with stereo-photomicrographic recording", Geofisica Pura e Applicata, Milano, Vol. 41, pp. 211-216 (1958).

REFERENCES (Contd.)

(42) Penndorf, R.B.: "New Tables of Mie-scattering Functions for Spherical Particles." Geophysical Research Papers No. 45; Geophysical Research Directorate, U.S. Air Force Cambridge Research Center, (1956).

(43) Volmer, M. and Flood, H.: "Tröpfchenbildung in Dämpfen", Z. phys. Chem. A, 170, p. 273 (1934).

(44) Mason, B.J.: "The Physics of Clouds", Clarendon Press, Oxford, p. 19 (1957).

(45) Leighton, P.A.: "The Photochemistry of Air Pollution", Academic Press, New York and London, p. 246 (1961).

(46) Dunham, S.B.: " Production of Nuclei by Chemical Supersaturation", Journal de Recherches Atmospheriques, Vol. 2, No. 2-3, p. 331 (1966).

(47) O'Connor, T.C., Sharkey, W.P.F. and O'Brolchain, C.: "On condensation nuclei produced at heated surfaces", Geofisica Pura e Applicata, Milano, Vol. 42, pp. 109-116 (1959

(48) Goetz, A. and Kallai, T.: "Design and performance of an aerosol channel for the synthesis and study of Atmospheric reaction products", APCA Journal, Vol. 12, No. 9, pp. 437-443, (1962).

(49) Goetz, A. and Pueschel, R.F.: "The Effect of Nucleating Particulates on photochemical aerosol formation", APCA Journal, Vol. 15, No. 3, pp. 90-95 (1965).

(50) Megaw, W.J. and Wiffen, R.D.: "The generation of condensation nuclei by ionising radiation", Geofisica Pura e Applicata, Milano, Vol. 50, No. 3, pp. 118-128 (1961).

(51) Junge, Christian E.: "Chemical Analysis of Aerosol Particles and of gas traces on the Island of Hawaii", Tellus, Vol. 9, No. 4, pp. 528-537 (1957).

(52) Hall, T.C., Jr.: "Photochemical Studies of Nitrogen Dioxide and Sulphur Dioxide", Doctoral thesis, University of California, Los Angeles (1953).

(53) Nolan, J.J. and Guerrini, V.H.: "The diffusion coefficients and velocities of fall in air of atmospheric condensation nuclei", Proc. Roy. Irish Acad., Vol. 43, A, pp. 5-24 (1935).

REFERENCES (Contd.)

(54) Nolan, J.J., Nolan, P.J. and Gormley, P.G.: "Diffusion and fall of atmospheric condensation nuclei", Proc. Roy. Irish Acad., Vol. 45, A, pp. 47-63 (1938).

(55) Pollak, L.W., O'Connor, T.C. and Metnieks, A.L.: "On the determination of the diffusion coefficient of condensation nuclei using the static and dynamic methods", Geofisica Pura e Applicata, Vol. 34, pp. 177-195 (1956).

(56) Fürth, R.: "On the theory of diffusion and resedimentation of condensation nuclei in cylindrical containers", Geofisica Pura e Applicata, Vol. 31, pp. 80-89 (1955).

(57) Kennedy, H.: "The large ions and condensation nuclei from flames", Proc. Roy. Irish Acad., Vol. 32, A, pp. 58-74 (1916).

(58) Nolan, P.J.: "The influence of condensation nuclei and dust particles on atmospheric ionisation", Proc. Roy. Irish Acad., Vol. 41, A, pp. 61-69 (1933).

(59) Nolan, P.J.: "Experiments on condensation nuclei", Proc. Roy. Irish Acad., Vol. 47, A, pp. 25-38 (1941).

(60) Nolan, P.J. and Kuffel, E.: "Coagulation and diffusion of enclosed nuclei", Geofisica Pura e Applicata, Vol. 31, pp. 97-106 (1955).

(61) Einstein, A.: Ann. d. Phys., Vol. 17, p. 549 (1905); Zs. f. Elektroch., Vol. 14, p. 235 (1908).

(62) Cunningham, A.: Proc. Roy. Soc. London, Vol. 83, A, p. 357 (1910).

(63) Millikan, R.A.: "Coefficients of slip in gases and the law of reflection of molecules from the surfaces of solids and liquids", Phys. Rev., Vol. 21, No. 3, p. 217 (1923).

(64) Millikan, R.A.: "The general law of fall of a small spherical body through a gas, and its bearing upon the nature of molecular reflection from surfaces", Phys. Rev., Vol. 22, pp. 1-23 (1923).

(65) Smoluchowski, M.: Z. physik Chem., Vol. 92, p. 129, (1917).

(66) Nolan, P.J. and Kennan, E.L.: "Condensation nuclei from hot platinum; size, coagulation coefficient and charge-distribution", Proc. Roy. Irish Acad., Vol. 52, A, pp.171-190 (1949).

REFERENCES (Contd.)

(67) O'Connor, T.C. and Flanagan, V.P.V.: "The measurement of size distributions in Aitken nuclei", Geofisica Pura e Applicata, Vol. 50, No. 3, pp. 60-66, (1961).

(68) Nolan, P.J.: Personal communication.

(69) Norinder, H. and Siksna, R.: "Ions produced in a room by ultraviolet light from a quartz-mercury arc and by an open electric heater", I.V.A., Vol. 23, No. 2, pp. 64-70 (1952).

(70) Norinder, H. and Siksna, R.: "Ions produced in the air at atmospheric pressure by ultraviolet light from a quartz-mercury arc", Arkiv for Fysik, Stockholm, Vol. 5, No. 23, pp. 471-491 (1952).

(71) Ministry of Labour, H.M. Factory Inspectorate, London: "Methods for the detection of toxic substances in air", Booklet No. 3, "Sulphur Dioxide", Her Majesty's Stationery Office, London (1961).

(72) McWilliams, S., and Morgan, W.A.: "The Relation between the concentration of atmospheric condensation nuclei, and other meteorological elements at Valentia Observatory" Geofisica Pura e Applicata, Vol. 31, pp. 129-146, (1955).

(73) Leighton, P.A.: "The Photochemistry of Air Pollution", Academic Press, New York and London, pp. 60-61, (1961).

(74) Thompson, B.A., Harteck, P., and Reeves, R.R.: "Ultraviolet absorption coefficients of CO_2, CO, O_2, H_2O, N_2O, NH_3, NO, SO_2, and CH_4 between 1850 and 4000A". Journal of Geophysical Research, Vol. 68, No. 24, pp. 6431-6436, (1963).

(75) Millipore Filter Corporation,: "Microchemical and Instrumental Analysis", Application Data Manual - 70, Millipore Filter Corporation, Bedford, Mass., U.S.A., p. 23 (1963).

(76) Mellor, J.W.: A Comprehensive treatise on Inorganic and Theoretical Chemistry, Vol. X., Longmans Green and Co. (1930).

(77) Gerhard, E.R. and Johnstone, H.F.: Indust. and Eng. Chem., Vol. 47, p. 972, (1955).

(78) Blacet, F.E.; J. Phys. and Colloid Chem., Vol. 52, p. 534, (1948); Indust. and Eng. Chem., Vol. 44, p. 1339 (1952).

REFERENCES (Contd.)

(79) Baranova, A.I.; Zhur. Priklad. Khim., Vol. 31, p. 167, (1958).

(80) Brasted, R.C.: "Comprehensive Inorganic Chemistry", Vol. 8, D. Van Norstrand Company Inc., Princeton, New Jersey, (1961).

(81) Newton Friend, J.: "A text-book of Inorganic Chemistry", Vol. 7, part 2, Charles Griffin and Co. Ltd., London.

(82) Junge, C.E.: "Facts and Problems of Chemical Composition of Condensation Nuclei in unpolluted and polluted atmospheres".

(83) Kaufman, F.; Proc. Roy. Soc., Vol. 247, A, p.123, (1958).

(84) Stevenson, H.J.R., Sanderson, D.E. and Altshuller, A.P.: "Formation of Photochemical Aerosols", Int. J. Air Water Pollution, Pergamon Press, Vol. 9, pp. 367-375, (1965).

(85) Cadle, R.D.: "Rates of Chemical Reactions in the subionospheric atmosphere", Journal of Geophysical Research, Vol. 68, No. 13, pp. 3977-3986, (1963).

(86) Junge, C.E. and Manson, J.E.: Jour. Geophys. Research, Vol. 66, p. 2163, (1961).

(87) Chagnon, C.W., and Junge, C.E.: Jour. Met., Vol. 18, p. 746, (1961).

(88) Byers, H.R.: "Elements of Cloud Physics", The University of Chicago Press, Chicago and London, (1965).

(89) Paton, J.: "Noctilucent Clouds", Meteorological Magazine, Vol. 93, pp. 161-179, (1964).

(90) Nolan, P.J. and Mac Cormaic, P.S.: "The Nuclei produced by Disruptive Discharge at a water surface", Geophysical Bulletin No. 7, School of Cosmic Physics, Dublin Institute for Advanced Studies, (1953).

(91) Nolan, P.J. and Kuffel, E.: "Metal point discharge nuclei, and the production of multiple charged ions from condensation nuclei", Geofisica Pura e Applicata, Milano, Vol. 36, pp. 201-210, (1957).

(92) Nolan, P.J. and O'Toole, C.P.J.: "The condensation nuclei produced by point discharge", Geofisica Pura e Applicata, Milano, Vol. 42, No. 1, pp. 117-126, (1959).

REFERENCES (Contd.)

(93) Nolan, P.J.: "Small nuclei produced by discharge at a point", Recent Advances in Atmospheric Electricity, Pergamon Press, London, (1959).

(94) Watson, A.A.: "An examination and possible exploitation of certain unexplored features in the operation of high pressure cloud chambers", Ph.D. Thesis, University of Edinburgh, Scotland, (1964).

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